GEOLOGY, DEVELOPMENT, & ECONOMICS OF ZEOLITE MINING IN AUSTRALIA

STEVEN ALAN COOPER
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Ca-clinoptilolite crystals growing into and replacing glass shards.
Thin section from Escott Zeolite Mine, Werris Creek, N.S.W.
Scale bar is approximately 50 μm.
Photograph courtesy of Prof. Hideo Minato

DECLARATIVE STATEMENT

To the best knowledge and belief of the writer, this thesis contains no work previously published, or written by another party, without having made due reference to them in the text of this thesis. Nor does this thesis contain material which has been accepted for the award of any other higher degree or graduate diploma at this, or any other, tertiary institution.

Steven Alan Cooper
15 December 1993

ABSTRACT

Zeolite mining in Australia has been developing at a steady, if slow pace since late 1987, when the first Australian zeolite mine commenced operation at Escott. This inaugural economic deposit, likely to be joined by others, is situated in altered ignimbrite, air fall pyroclastic, and volcaniclastic lacustrine sediments of the Late Carboniferous Currabubula Formation in north-eastern New South Wales. The Early Carboniferous Ducabrook Formation of the Drummond Basin in central Queensland is another zeolite deposit with good economic potential. While generally the regional geology for each deposit is relatively simple and understood, characterisation of the zeolitic mineralisation has been determined by a wide range of geochemical, petrological, physical, SEM, and recently thermal XRD and nuclear magnetic resonance (NMR) methods. Studies have confirmed that the prominent zeolite mineral mined at Escott is low thermal stability Ca-clinoptilolite, and that this zeolite mineral is likely at the other prospects.

This characterisation is important as the natural zeolitic rock produced has physical properties (density, hardness, age, etc.) different from most overseas zeolitic rocks, thereby requiring specific trials to be developed to examine the application of its different properties. Also, different deposits show physical and chemical variations that might play an unknown part in performance for particular markets. The aim of this study is to compile and obtain new information of the characterisation of the Australian natural zeolites, in the manner outlined by Sheppard (1983). Such determination is essential for establishing a rational basis for the commercial use and application research of natural zeolites. No systematic compilation or examination had been made to date on the increasingly large amount of laboratory and exploration material collected over six years. It is hoped that this thesis provides a reference source, both for geological and other disciplines utilising zeolites. A starting point for any new zeolite deposit is the established characterisation methods for natural zeolitic rocks developed by the New South Wales Department of Mineral Resources (Fredrickson, 1986).

Sale and marketing information gained in Australian over its six year history has shown the importance of working with clients, and the development of innovative technology for the utilisation of natural zeolites (Stephen & Gout, 1993). Product development has ranged over packaging, particle sizing and selective high grade mining, with strong encouragement for bilateral communication with potential clients during trialing. Main barriers to expanded growth in some markets are milling and freight costs, which are currently being addressed. Future developments will include chemical and physical modification of the natural zeolite to meet

certain client requirements. One threat to market development is the potential health implications of the fibrous zeolite erionite currently mined overseas.

The natural zeolite industry in Australia is established, with total invoiced sales to date of over a million dollars, but growth is slow and difficult due to volume related inefficiencies resulting in high costs and slow consumer appreciation of the products. Geological studies have been minimal due to the need for low cost development, but this has changed with the realisation that detailed characterisation is essential. The role of the geologist has thus also changed, from that of active exploration, to technical coordinator for a mineral group with extremely wide product applications.

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1. INTRODUCTION

Zeolite mining in Australia commenced in December 1987 as a 15 tonne test bulk sample taken at Escott, New South Wales. Subsequently, similar to most non-communist zeolite deposits, growth and development has been slow and steady. Much of this trend can be attributed to the lack of an existing market, combined with lack of experience, both on the part of the producer and of the consumer, in dealing with and utilising natural zeolites.

This thesis summarise the geological setting, exploration techniques, production, marketing and the sale of natural zeolites in Australia. It presents a case study of a completely new mineral product that has been launched into a sophisticated market environment by a single mining company. This has generated problems not normally encountered in mining and associated marketing. The geology and mineralogy are sufficiently different from current zeolite production in overseas countries to make it necessary to precisely characterise each zeolite occurrence. Until recently, minimum effort was devoted to documenting the geology and characteristics, because the major efforts were directed at market development. Sheppard (1983) outlined the problem of the lack of zeolite characterisation, and it is hoped that this thesis goes towards addressing this area.

The reliance on overseas trials for predicting the potential uses has been hampered by the lack of published papers, that actually give characterisation details about the zeolitic materials being trialed or tested. As will be shown, without details on a range of other variables, comparisons of quoted Cation Exchange Capacities (CEC)[1], for most applications are not possible. Yet cation exchange capacity is the so-called standard measure of grade for zeolite deposits. This has all combined to make comparisons between zeolite deposits very difficult for the consumers.

2. GEOLOGY OF AUSTRALIAN ZEOLITE DEPOSITS

The literature abounds with papers detailing trials in agriculture and animal feed, plus some geological papers, that often give only a zeolite mineral species name, and maybe a chemical analysis (through often what exactly is assayed is not specified) concerning the zeolitic product under discussion (Sheppard, 1983). The same can be said of the standard measurement of usefulness of zeolites, the CEC, but this measurement is often not even quoted. For tests to be comparative and useful, more information is required regarding the zeolitic mineral or rock being used.

[1] The CEC is a relative measure of the number of cations present within a zeolite crystal available for exchange.

This chapter attempts to provide a characterisation of Australian zeolites so as to assist other professions in their trials and studies. The following criteria are desirable for characterisation (modified from Sheppard, 1983);

1. Zeolite species name,
2. Suppliers name, address, product code,
3. Deposit name and location,
4. Particle sizing used (in millimetres),
5. Mineralogical composition of zeolitic material,
6. Chemical analysis of the zeolite mineral and material,
7. Homogeneity of the zeolitic material,
8. Crystal size and habit of zeolite,
9. Cation exchange or adsorption properties, and measurement method,
10. Any modifications to natural zeolite product.

In the following discussions, samples referred to as zeolitic are those with an Ammonia Exchange Capacity (AEC)[2] greater than 70 meq/100 g[3], unless zeolite content has been confirmed by other procedures. Experience shows that above this arbitrary value (after checking smectite or kaolinite contents are insignificant) there must be a reasonable proportion (>20%) of zeolite minerals (Fredrickson & Dowswell, 1988).

2.1 ZEOLITE PROVINCES IN AUSTRALIA

Four authigenic Zeolite Provinces are currently known within Australia (Fig. 1). The first embraces Late Carboniferous rocks in the Tamworth Belt of north-eastern New South Wales (Flood & Taylor, 1991). The second covers the Early Carboniferous rocks from the Drummond Basin in central Queensland. The third Early Cretaceous rocks from the Otway Basin, western Victoria. The fourth documented area is in central Australia, and consists of an example of zeolites forming in Tertiary-Quaternary saline, alkaline lake deposits.

TAMWORTH BELT ZEOLITE PROVINCE

The Tamworth Belt Zeolite Province, as described by Flood & Taylor (1991), extends for 290 kilometres and is composed of Late Carboniferous volcanic braided stream conglomerates. Thin and widespread silicic ignimbrite sheets and are typical of the Province (McPhie, 1986). Zeolite

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2 AEC is a method of determining the CEC by using ammonia as the measured exchanged cation.

3 The unit of measurement for CEC and AEC is millieqivalents per 100 grams (meq/100 g).

seems to be restricted to silicic tephra units, generally associated with lacustrine or interpreted water-associated environments. Numerous units are known, but generally thickness is too thin (<2 metres), or too low grade (<120 meq/100 g) for commercial development. Currently one site is being actively mined (Escott), another planned (Sheedy), and a third site under consideration (The Gap).

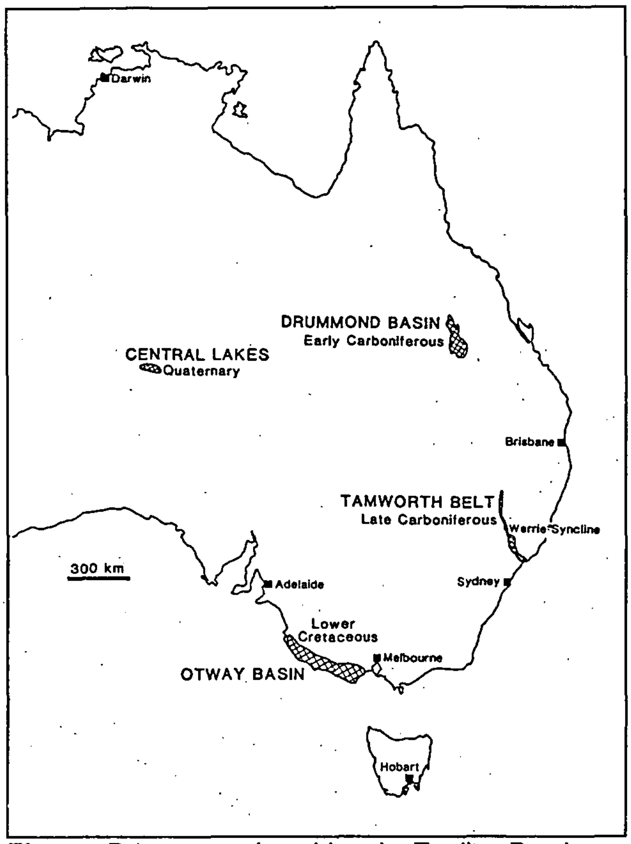


Fig. 1 Documented authigenic Zeolite Provinces in Australia.

DRUMMOND BASIN ZEOLITE PROVINCE

The second Province also contains non-marine, water-lain silicic tephra sheets. These shallow-dipping, gently-folded units within the Early Carboniferous (Visean) Ducabrook Formation outcrop in the eastern Drummond Basin and are zeolitised. During 1988, an independent exploration company, Burgundy Exploration Pty Ltd (Harms, 1990), provided Zeolite Australia Limited with a suite of samples that physically resembled hand specimens of zeolite currently mined at Escott. Testing by Zeolite Australia confirmed high AEC and zeolitic mineralogy.

Generally the tephras are relatively flat-lying units interbedded with feldspathic-lithic sandstones and green mudstones of the Ducabrook Formation. The depositional environment is non-marine and shallow water (Drysdale, 1992), with indications of glacial conditions (Pinchin, 1978), within a back-arc setting (Johnson & Henderson, 1991). The area of known zeolitic outcrop is a 130 kilometre belt running from exposures located in the Mistake Creek syncline, west of Claremont, south-east to within various local synclines, south of the township of Anakie. Generally the units are thin and not well exposed, but units south-west of Anakie, in the Willows area, have economic potential.

OTWAY BASIN ZEOLITE PROVINCE

The third Province, the Lower Cretaceous Otway Group within the Otway Basin, has been well documented by Duddy (1983). He outlined the distribution of clinoptilolite-heulandite within pores representing up to 10-15 percent of this fluviatile volcaniclastic sequence. The Otway Group, over 1200 m in thickness and extending 800 kilometres, is not expected to be economic due to the lack of higher grade zeolitic material within the sequence, together with the lack of outcrop. The Otway Group is conspicuous for its lack of primary volcanic material, yet the sandstones and mudstone sequence is composed of material derived from contemporaneous pyroclastic volcanism (Duddy, 1983). While chemical and thermal conditions were suitable for uniform zeolite formation over a large interval, the sediments were composed of too much lithic and crystal material to form other than low grade zeolites.

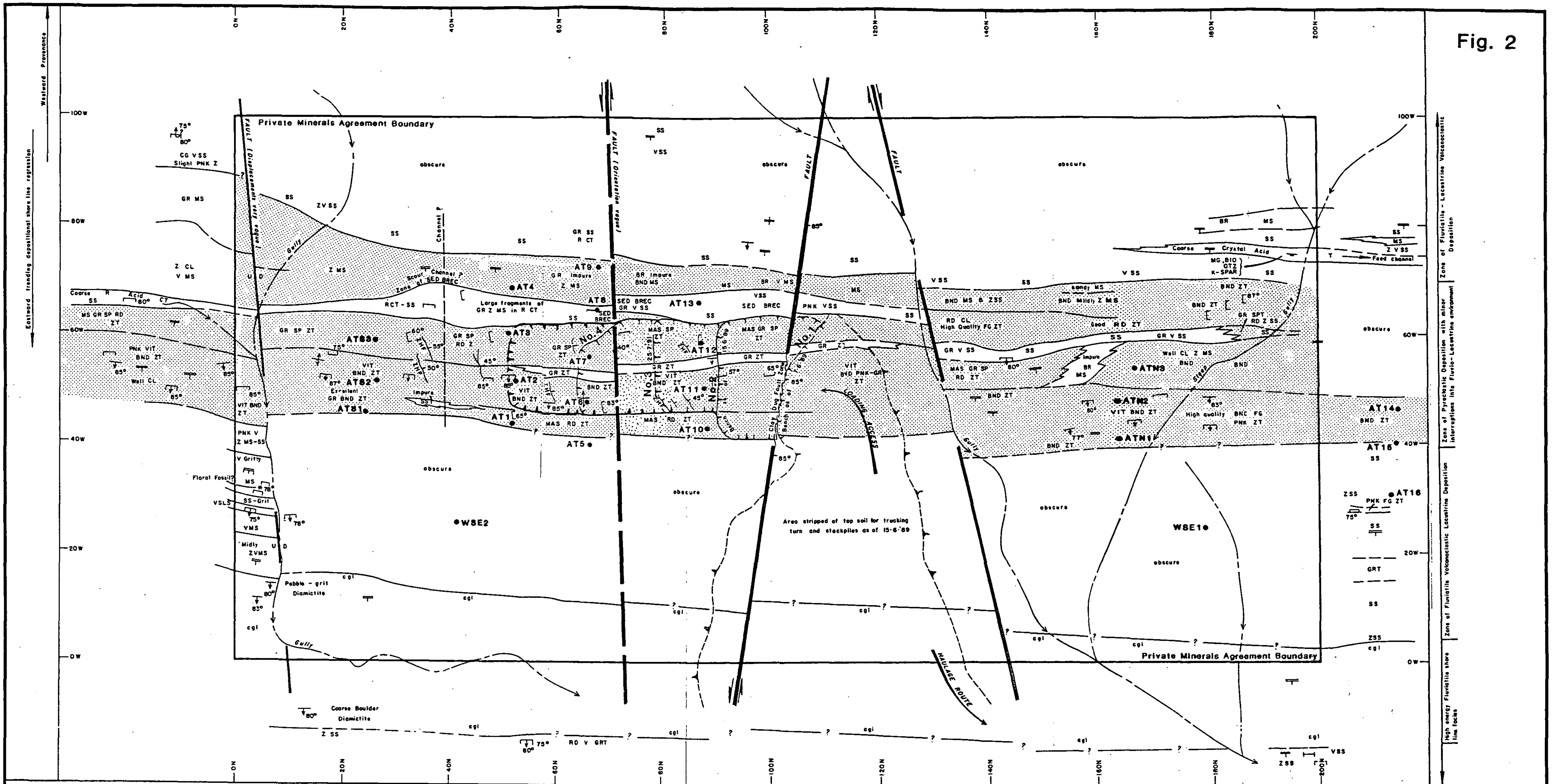
CENTRAL AUSTRALIA LAKES ZEOLITE PROVINCE

The same lack of siliceous feed material is probably the reason that the zeolitic content (around 10%) of the current saline-alkaline lakes in central Australia, the fourth province, is low. The formation and distinctive features of saline-alkaline lake zeolite deposits are well documented by Surdam (1977), and Surdam & Sheppard (1978). Arakel (1987), published the first description of Australian zeolites in this setting within authigenic pore fillings in a dolomitic groundmass beneath current saline lakes near Curtin Springs, Central Australia (Fig. 1). Dominant zeolite mineral is analcime, with minor phillipsite, mordenite and chabazite. However, "the possibility of a commercial zeolite deposit is increased by a high content of glass and a low content of crystal and rock fragments" (Sudam & Sheppard, 1978, p.172). It is apparent that most of central Australia lacks abundant volcanic glass content. Thus while the chemical environment is favourable for zeolite formation, generally the playa lakes lack sufficient siliceous material to generate high grade zeolite deposits.

2.2 ESCOTT NATURAL ZEOLITE MINE, NEW SOUTH WALES

At Escott the unit mined occurs within the Currabubula Formation, south west of the township of Werris Creek. The unit was first mapped by geology students from the University of New England, Armidale, with sampling by the New South Wales Department of Mineral Resources later confirming the zeolitisation (P. Flood, personal communication). The area being mined is within a Private Minerals Agreement (PMA) area (Fig. 2), surrounded by a larger Mining Lease Application (MLA 212, Fig. 3). Following an initial two deep drillholes (Flood, 1987), the deposit was subsequently costeaned and air-track drilled to confirm the tonnage and grade, and a 15 tonne bulk sample was then collected. Later detailed mapping was completed by contract geologist R. Hill (Fig. 2) within the PMA area.

Fig. 2



- Bedding facing overturned
- Bedding strike and dip and facing
- Bedding strike and vertical
- Cleavage trend and dip
- Strike and dip direction
- Quarry bench A
- Steep slope - bank
- Drainage
- Fault (Approx. position)
- Shear
- Fault - up/down slip
- Joint and dip
- Cleavage trend and vertical
- Strike of bed
- Fracture plane
- Quarry bench B
- Disturbance boundary
- Unit boundary (Approx. boundary)
- Questionable boundary
- AT14 Air track hole N - North S - South
- WSE1 Percussion hole

Z	Zeolitic	MS	Mudstone	FG	Fine grained
cgl	Conglomerate	SED	Sedimentary	MG	Medium grained
V	Volcanoclastic	BREC	Breccia	CG	Coarse grained
VIT	Vitreous	SS	Sandstone	SP	Speckled
GRT	Grits	QTZ	Quartz	SPT	Spotted
BND	Banded - finely bedded	PNK	Pink	T	Tuff
SSD	Soft sedimentary deposit	RD	Red	MAS	Massive
ZHF	Zeolite healed fracture	BR	Brown	BIO	Biotite
R	Reworked	GR	Green	K-SPAR	Potash feldspar
CT	Crystal tuff	CL	Cleaved		

GRID NORTH
MAG. NORTH

0 10 20 30
metres

Geology by R. Hill

ZEOLITE AUSTRALIA LIMITED

ESCOTT ZEOLITE DEPOSIT

GEOLOGY

PRIVATE MINERALS AGREEMENT AREA

N 403

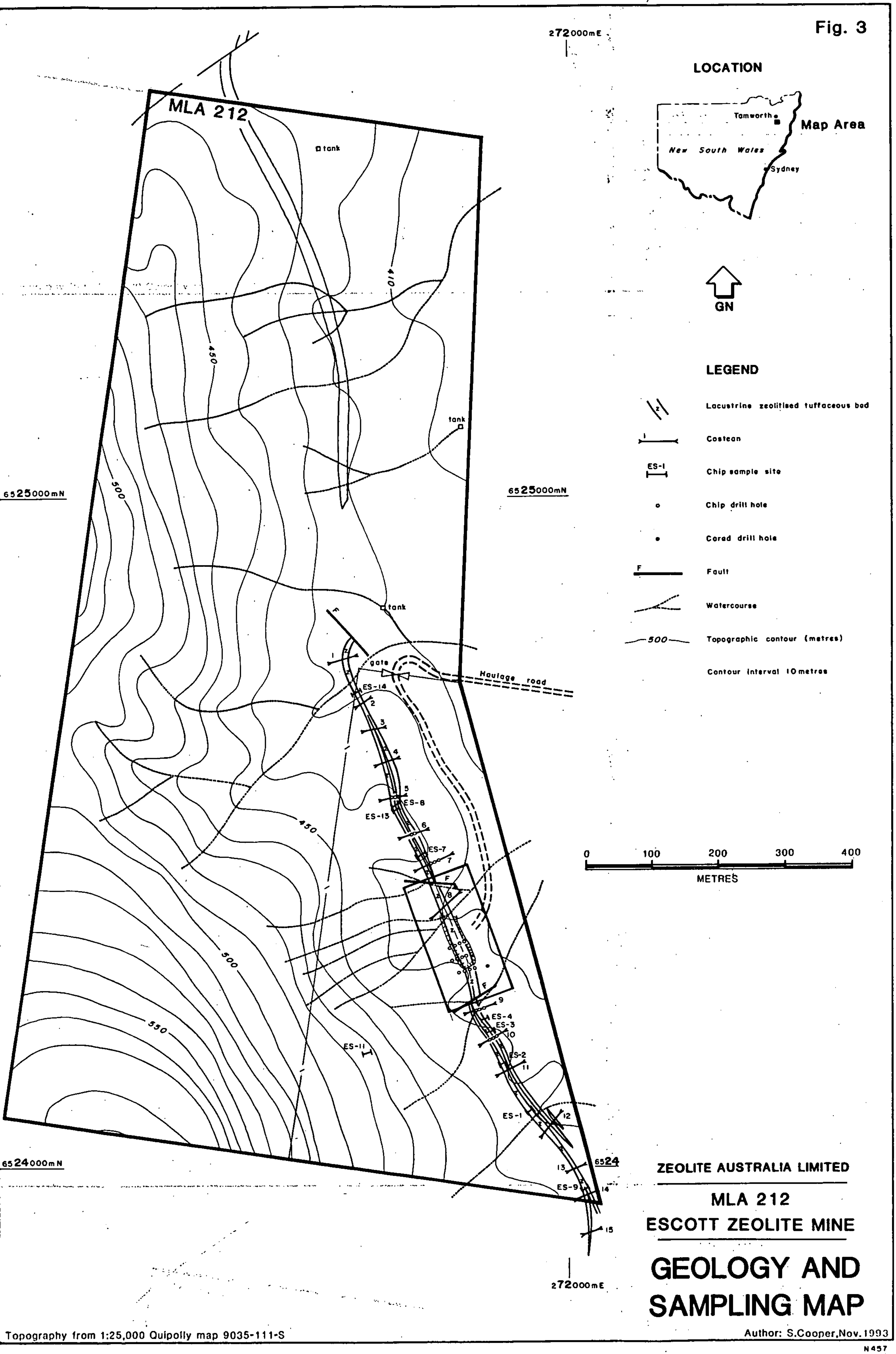


Fig. 3
LOCATION
Tamworth
Map Area
New South Wales
Sydney
GN
LEGEND
Lacustrine zeolitised tuffaceous bed
Costean
Chip sample site
Chip drill hole
Cored drill hole
Fault
Watercourse
Topographic contour (metres)
Contour interval 10 metres
0 100 200 300 400
METRES
272000mE
6525000mN
6524000mN
MLA 212
tank
gate
Haulage road
410
450
500
550
ES-1
ES-2
ES-3
ES-4
ES-7
ES-8
ES-9
ES-11
ES-13
ES-14
ZEOLITE AUSTRALIA LIMITED
MLA 212
ESCOTT ZEOLITE MINE
GEOLOGY AND SAMPLING MAP
Topography from 1:25,000 Quipolly map 9035-111-S
Author: S.Cooper,Nov.1993
N457

The sequence has only been mapped in detail around the mine (R. Hill, unpublished map, 1989). The extensions north and south have been mapped in a reconnaissance manner only. The western basal sequence to the area is coarse fluviatile volcaniclastic sandstones, overlain by green weakly zeolitic lacustrine mudstone (Flood, 1991). This is overlain by pink volcaniclastic sandstone displaying basal scour channels and abundant basal clasts of the underlying mudstone. The next unit is mappable for some distance and consists of a massive, red with green speckles, zeolitised vitric air- fall tuff, 5 to 7 metres thick. This is termed Unit *A* by Flood (1991) and thin section petrography confirms uniform grain size. Unit A has a thin green zeolitic unit lying above reworked volcaniclastic sands; it wedges out to the south. The next unit, Unit *B,* is a laminated mudstone with 1 to 5 mm thick normal graded beds showing individual grading from red at the base, to green in the uppermost layers. The thin layers also display planar and current cross bedding and bioturbation. This is followed by a four metre thick red, crystal vitric air-fall tuff, Unit *C*. This is overlain by Unit *D*, a pink volcaniclastic mudstone to fine sandstone, together with gritty sandstones and mildly zeolitic volcanic mudstones. Near the eastern margin of the Private Mining Agreement Area the coarsening up sequence becomes a pebbly diamictite, grading still further to coarse boulder diamictite, before disappearing below the black soil. All contacts appear conformable. The units mined are A and B. Zeolitisation has replaced both glass shards and the fine groundmass within most units, with lower grades being due to excessive crystal fragments.

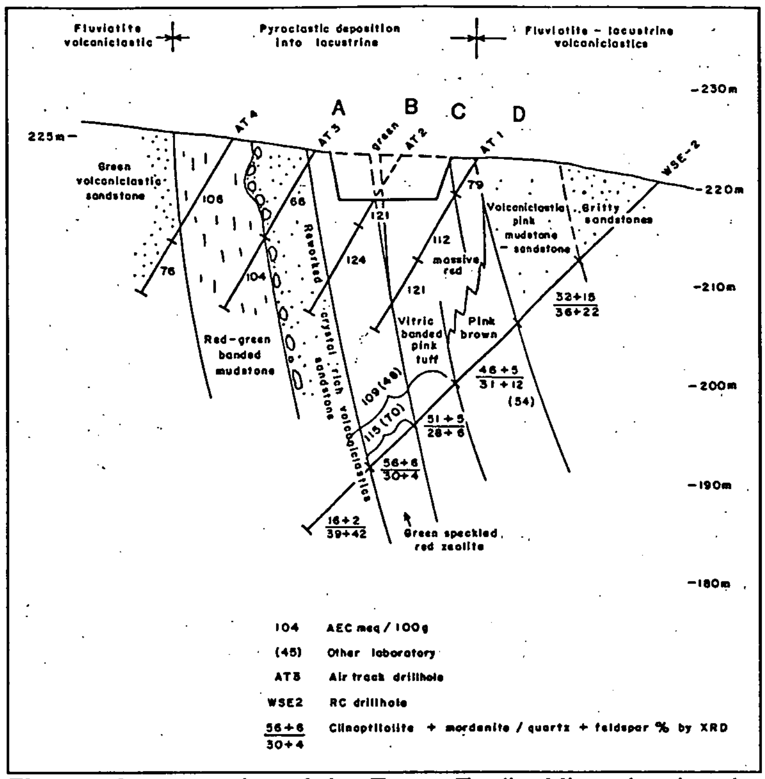


Fig. 4 Cross section of the Escott Zeolite Mine showing the main units involved, and AEC grades measured along drillholes.

MINERALOGY

XRD studies (Fredrickson & Pecover, 1987) showed the mineralogy of Escott as dominant quartz, moderate clinoptilolite, and small amount feldspars. Flood & Taylor (1991) confirmed that the mined section contains 60 percent zeolite (minor mordenite), 30 percent quartz, 4 percent feldspar, trace amount biotite and clays. The ratios for drillhole WSE-2 are shown in Figure 4.

Microprobe analysis and detailed microscopy have shown that the interior of the large shard pseudomorphs is composed of relatively large, blocky crystals of Ca-clinoptilolite. Mordenite is present in the Fe-enriched rims of the replaced shards (Flood, 1991, see frontispiece photograph), and the Ca-clinoptilolite appears to have grown inward from this layer. An SEM picture of the thin, monoclinic zeolite crystals is provided in Figure 5.

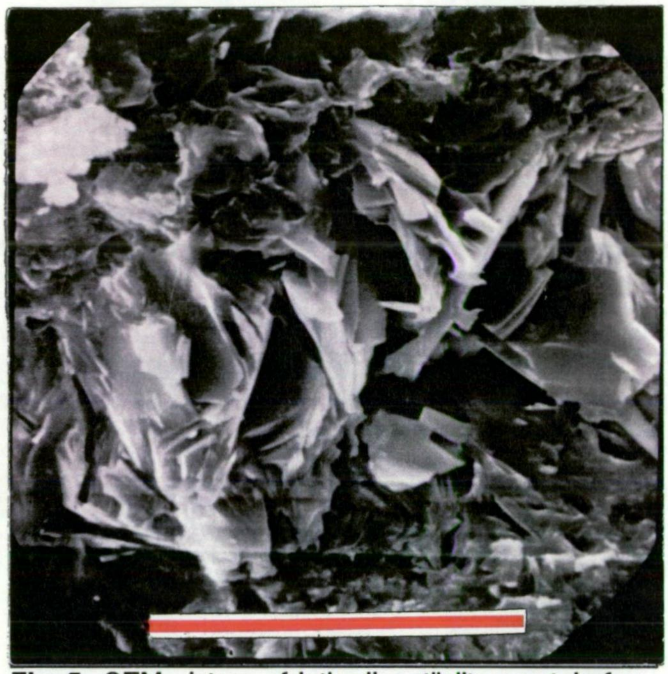


Fig. 5 SEM picture of lath clinoptilolite crystals from Escott. Normally the crystals are not so well developed. Scale bar 0.05 mm.

Numerous thin sections supplied by P. Flood have shown that phenocrysts including quartz, albite, orthoclase (sanidine), and smaller biotite flakes, are present in a glass shard dominated background. The quartz is mainly angular and widely distributed in the air-fall tuffs.

CLINOPTILOLITE AND HEULANDITE

Heulandite was proposed by Brooke (1822), and clinoptilolite by Schaller in 1932. The two are close to isostructural, therefore confusion has resulted in the nomenclature (Gottardi & Galli, 1985). It has even been proposed that the name clinoptilolite be discontinued (i.e. Tschernich, 1992). Which mineral present is important as most research for commercial applications is performed using clinoptilolite, and to have heulandite would cause confusion for those with little mineralogy. The Heulandite Group (Gottari & Galli, 1985) has the general formulae of $(Ca,Na_2,K_2,Mg,Ba,Sr)_8(Al_8,Si_{28},O_{72}).24H_2O$ (Tschernich, 1992), and are monoclinic. Clinoptilolite is now considered one of the most common authigenic silicates to be found in sedimentary rocks (Mumpton, 1978).

A common method of chemical definition proposed by Mason and Sand (1960) requires that clinoptilolite have Ca<(Na+K). Gottari & Galli (1985) also accepted the nomenclature of Mason

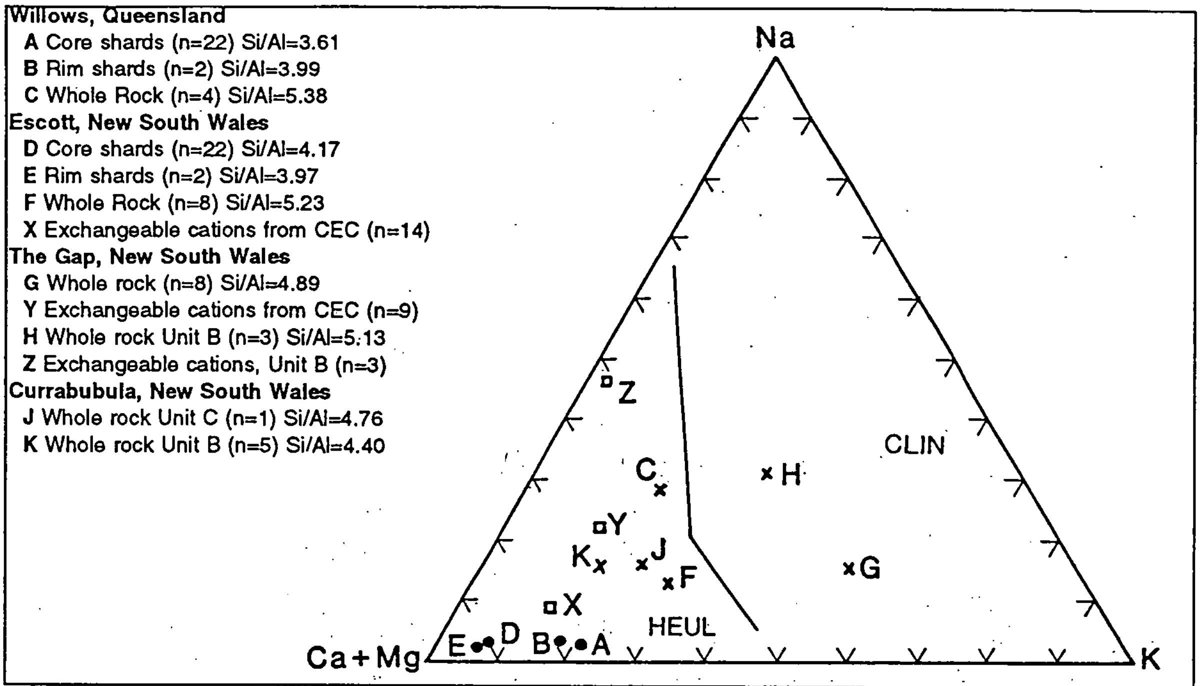


Fig. 6 (Ca+Mg)-Na-K summary plot of microprobe crystals ●, whole rock **x**, and exchangeable cations □ for N.S.W. and Queensland sites.

& Sand and define clinoptilolite with (Ca+Sr+Ba)<(Na+K). Minato & Utada (1970) use the major cation ratios, with separation based on the tertiary diagram (Ca+Mg)-K-Na (Fig. 6). It is now accepted that there is a complete spectrum of alkalis within clinoptilolite and heulandite (Birch, 1989; Tschernich, 1992), and that separation based on alkalis alone is not justified.

Another method used to chemically distinguish clinoptilolite is based on Si/Al ratios. Boles (1972) requires clinoptilolite to have Si/Al > 4.0, while Ming & Dixon (1986) provided a similar definition of clinoptilolite as having Si/Al ratio of 4.3 to 5.3, compared with heulandite 2.5 to 3.7. The Si/Al mean ratios for Australian zeolite, both of whole rock and zeolite crystal microprobes, is provided with Figure 6.

A physical method of distinguishing microcrystalline heulandite from clinoptilolite, and the definition accepted by many authors (Gottardi & Galli, 1985), was the thermal method proposed by Mumpton (1960), which involves heating to 400°C and using XRD to check for destruction of heulandite. Later this was shown to be correlated with the major cations present (Alietti et al., 1974), Ca-clinoptilolite having a low thermal stability close to heulandite. Minato & Utada (1986) believe that Si and Al are involved in cation exchanges, and that the thermal difference is related to the Si/Al crystal ratio.

Minato & Utada (1986) provide the follow distinguishing features of clinoptilolite, compared to heulandite;

1. Genesis: clinoptilolite is diagenetic and found in sedimentary-tephra rocks by the alteration of volcanic glass or fills grain boundaries. Heulandite is not only in sediments, but also in vugs and hydrothermal veins in basaltic and andesitic rocks.
2. Optical Properties: clinoptilolite has refractive index lower than 1.484, and heulandite is higher than 1.488. One of the characteristic features of clinoptilolite is its microcrystallinity (Gottardi, 1978), and this makes optical properties hard to determine.
3. Chemical: clinoptilolite is more alkalic and more silicic than heulandite. Minato & Utadu (1986) suggest that Al and Si are possibly involved in cation exchanges.
4. Crystal Structure: Both have similar crystal structure, but clinoptilolite does not transform into B-type, regardless of exchangeable cations.

When using chemical composition for identification, it is often not clear whether many published assay values are microprobes of the zeolite crystals, or other analytical methods on zeolite concentrates, or are whole rock analyses, the last two naturally containing other impurities. The plot of whole rock chemistry is very different from that observed for microprobe analysis of zeolite crystals as can be clearly seen in Figure 6, where both crystal and whole rock means are plotted.

Current study involving both thermal XRD and experimental NMR on Escott samples, combined with the distinguishing features listed by Minato & Utada (1986), confirm that the zeolites are predominantly Ca-clinoptilolite.

GEOCHEMISTRY

Assays of whole rock samples have been completed on many samples of zeolitic rocks. For the zeolitic rocks from the Currabubula Formation, a useful suite of comparison analyses is provided by the twenty-two samples of relatively unaltered rhyolite ignimbrite from the Currabubula Formation (and from the same 1:100,000 Tamworth 9035 map sheet) by McPhie (1984). As these unaltered samples, and the zeolitic samples, are part of the same eruptive sequence (McPhie, 1983), it will be assumed that there is a cogenetic relationship between them. Some of the samples by McPhie (i.e. Nos. 9, 10, 28, & 29) do show signs of alteration reflected chemically in low Si, high Ca, and Loss On Ignition (LOI) values greater than 5 percent, which could indicate calcite alteration (Davidson & Dashlooty, 1993), or slight zeolitisation (see below).

Thirty samples from the Currabubula Formation with AEC greater than 70 meq/100 g (most analysis are from Fredrickson & Pecover, 1987, combined with additional samples from Escott,

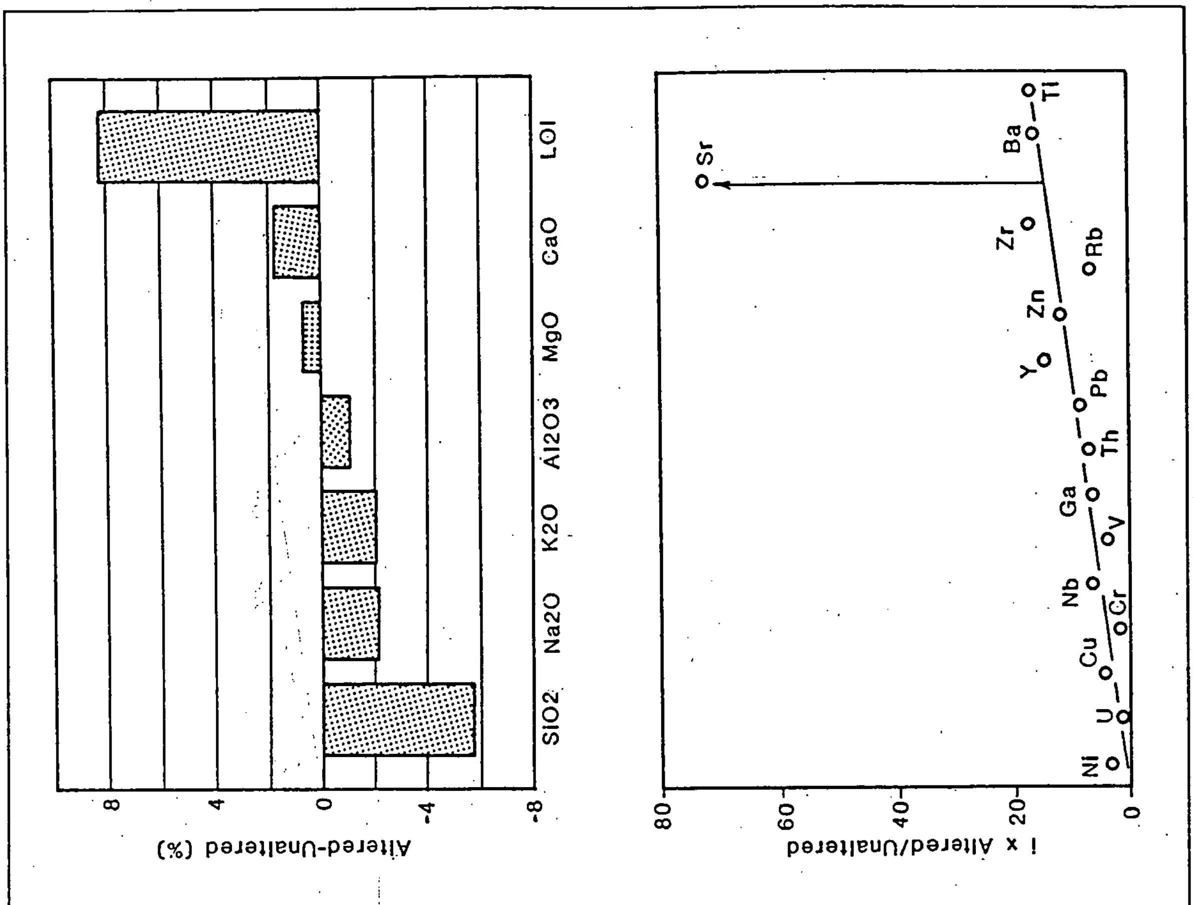


Fig. 7 Changes in means for the major oxides, and isocon plot for trace element means, showing changes with zeolite alteration from McPhie (1984, n=22) samples compared to selected zeolite samples (Appendix 1, n=30).

The Gap, and Currabubula, Appendix 1) were compared with the twenty two unaltered samples (McPhie, 1984, see Appendix 3). Inspection of the means (Fig. 7) and standard deviations show that the alteration of the tephra rocks have resulted in large increases in LOI, from normally below 3 percent, to over 10% after zeolitisation, reflecting large hydration (H_2O comprises over 90% of LOI) and is closely correlated with AEC grades (Fig. 8), and increases for both CaO (mean 1.1 to 2.8%) and MgO (mean 0.3 to 0.9%). These metasomatic increases were compensated by a significant (5.8%) decrease in SiO_2 (mean 73.9 to 68.1%), large decrease in Na_2O (3.4 to 1.3%) and K_2O (4.1 to 2.0%), together with a minor decrease in Al_2O_3 (mean 1% loss). The mean and standard deviation for TiO_2 were the same for both data sets in total, but does show variation between sites. These changes all reflect the alteration resulting from the major formation of Ca-clinoptilolite.

Trace elements show less variations. An examination was made of 16 elements (Fig. 7, isocon plot based on Grant, 1986, but elements arranged in order (i) of increasing mean concentration) from the unaltered data set by McPhie, and 30 samples of zeolitic (AEC >70 meq/100 g,

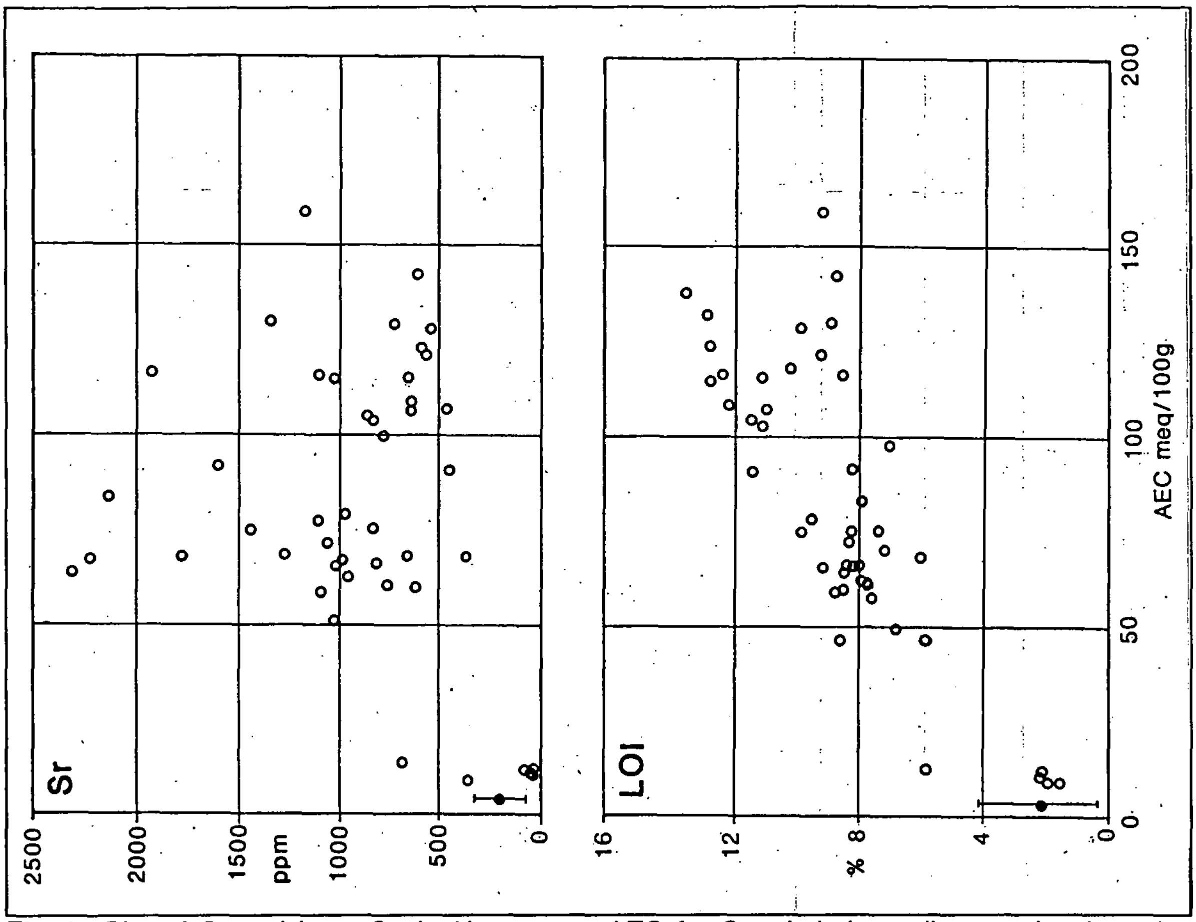


Fig. 8 Plot of Sr and Loss On Ignition verses AEC for Currabubula zeolite samples (samples from Fredrickson & Pecover, 1987). Mean and standard deviation shown on left side for McPhie (1984) unaltered samples.

Appendix 2) tephra from the Currabubula Formation (again most samples from Fredrickson & Pecover, 1987). The only element showing significant variation over standard deviations is Sr with an increase in mean (standard deviation) from 188 (119) to 970 (433) ppm. Examination of some minor trace metal variations show that drilling and milling increase some metals (i.e. Ni) compared with the rock chip samples.

That clinoptilolite rocks are often high in Sr is recorded, an example is the 80% clinoptilolite rock from Mud Hills, California, which contains 3720 ppm Sr (Lewis et al., 1983). Duddy (1983) discusses the source of Sr, and its concentration in many clinoptilolite deposits, which relies on a vertical migration and concentration of Sr due to albitisation and laumontisation alteration not retaining Sr. This does not appear to be the case within the Currabubula Formation (or the Queensland Ducabrook Formation (mean 2330, standard deviation 440 ppm Sr, from four samples with AEC >100 meq/100 g). It is suspected that the Sr is involved with the initial zeolitisation fluids early on, rather than cation exchange at a later higher alteration front. All Currabubula Formation low AEC samples, including the McPhie data set, have consistently low

	(ppm)		(ppm)
Ag	<2	Lu	0.64
As	11 (1)	Mn	222 (134)
Au	<0.03	Mo	<5
B	<100	Nb	14 (4)
Ba	884 (642)	Nd	37 (4)
Be	3.8 (2.9)	Ni	2.3 (1.0)
Bi	<2	Pb	20 (7)
Cd	<5	Pr	11
Ce	77 (8)	Rb	60 (26)
Cl	<100	S	<400
Co	<2	Sb	3.9 (1.2)
Cr	3.1 (3.5)	Sc	4.1 (1.1)
Cs	5.5 (0.8)	Sm	8.85
Cu	6.1 (6.0)	Sn	4.9 (2.5)
Dy	8.35	Sr	770 (267)
Er	5.21	Tb	1.23
Eu	1.50	Th	17 (3)
F	123 (57)	Tm	0.71
Ga	14 (2)	U	3 (1.3)
Gd	8.75	V	11 (3)
Hf	<3	Y	46 (13)
Hg	0.02 (0.01)	Yb	4.80
Ho	1.55	Zn	54 (17)
La	36 (5)	Zr	212 (38)
Li	14 (2)		

TABLE 1. Trace element means (standard deviation) for Escott Natural Zeolite whole rock. Constructed from 12 samples, but not all samples were assayed for the complete range (i.e. n<<12 most elements). Some values from Fredrickson & Pecover (1987).

Sr content, whereas with increasing AEC, the Sr concentration increases, but in a random manner (note large standard deviation, see Fig. 8). It is suggested that the zeolites are scavenging Sr, the random nature reflecting uneven supply of Sr for exchange. That both Sr and Ca show increases is not surprising considering the affinity the two elements have.

Given the mobility of the major elements, the relative immobile elements used by the Winchester & Floyed (1977) Zr/Ti-Nb/Y plot is employed to confirm the original rhyolitic nature of the zeolitic rocks. Figure 9 shows this plot with the three principal zeolitic locations within the Currabubula Formation, Escott, The Gap, and Currabubula near Spring Creek, together with four samples from the Willows in the Drummond Basin, and the 22 analyses for unaltered rhyolitic ignimbrites from the Currabubula Formation by McPhie (1984). Individual zeolite deposits do cluster around slight variations in TiO_2, but as the units are at different stratigraphic levels reflecting different eruption events, this difference is to be expected. This clustering is also observable within the data by McPhie. All the zeolitic samples plot within the rhyolite field, compared with the unaltered samples, which show a distribution just entering the rhyodacite field.

At the mineral scale, microprobe work using the Cameca electron microprobe at the Australian National University (Flood & Taylor, 1991), and recent work at the University of New England by P. Flood, have shown consistent compositions within altered shards from Escott and Willows. The groundmass, different from the shards, also displays uniformity between analyses. The positions of the altered shard cores and rims are plotted in Figure 6. The problem is that electron microprobe analysis of zeolites can be difficult, mainly due to the ease with which structural water, and sodium are boiled and lost by the electron beam (Birch, 1989). Indeed the microprobe analysis of the shard core and rims from Escott and the Willow site all fall outside the ratio criteria of [Al_2O_3+Fe_2O_3] : [MgO+CaO+Na_2O+K_2O] within 5 percent used by Surdam & Sheppard (1978) to indicate acceptable analyses. These analyses also do not conform to the charge balance error formula within 10 percent used by Birch (1978) for pure zeolite crystals. Thus, these analyses are considered only generalised analyses, and deviations from the idealised zeolite formulae caused by minor amounts of other minute minerals, together with the inherent difficulties with microprobing of microscopic zeolites, is to be expected.

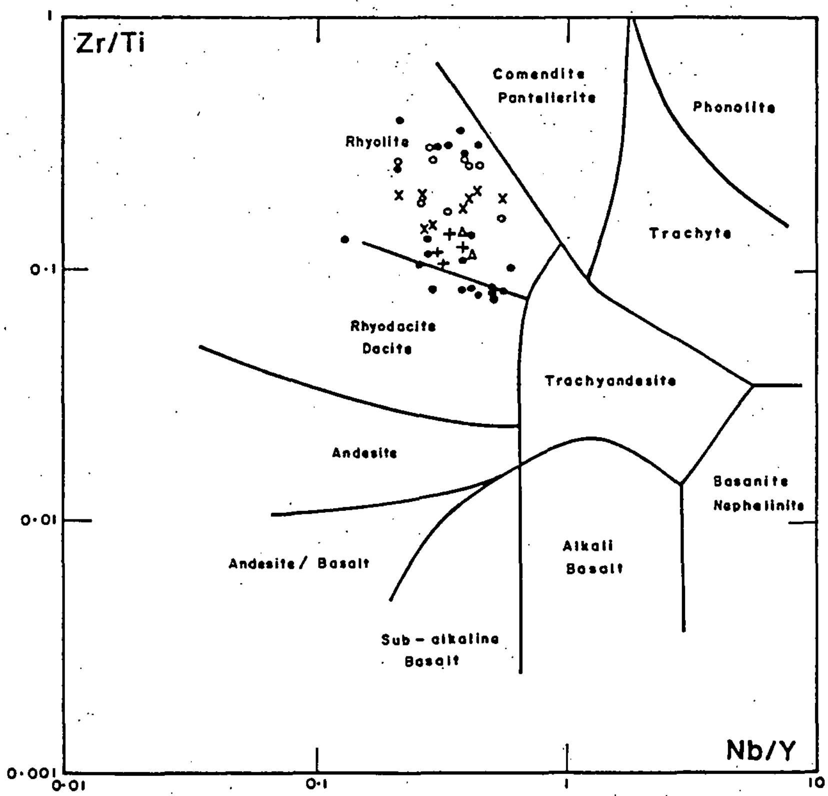


Fig. 9 Zr/Ti-Nb/Y plot of Currabubula Formation rhyolite ignimbrite (•, McPhie, 1984, n=22) compared with zeolitised samples from Escott (o, n=9), Sheedy site (△, n=2), The Gap (x, n=8), and Willows (+, Qld., n=4).

Microprobe analysis confirms the back-scattered electron images (fig. 6 of Flood & Taylor, 1991) which indicate that the potassium distribution is concentrated in the groundmass and the calcium is preferentially localised in the zeolitic shards (core mean 4.80% CaO), especially towards the peripheral portions (rim mean 4.98% CaO).

Being able to exchange cations depending on the environmental potential without altering the crystal structure makes zeolites useful, but difficult to characterise chemically. This is compounded by the fact that whole rock analyses of ignimbritic rocks generally do not represent primary magma composition due to volcanic fractionation by crystal concentration and pumice mixing, together with contamination by lithics from the vent walls and the ground surface. Thus, any interpretation of the zeolite bearing tephra chemistry must be made with these considerations in mind.

AEC AND CEC DETERMINATIONS

The exchangeable cation content of a zeolite needs to be known as it often influences the final determination of potential use. Indeed zeolites with high dominant exchangeable sodium should not be used with plants that are very sensitive to salt. Another example is clinoptilolites with a low potassium content, which seem to have high ammonium exchange capacity, making them good for agricultural applications. While high potassium clinoptilolites have a low ammonium exchange capacity, apparently because potassium is difficult to exchange out of clinoptilolite (Sheppard, 1983; see also Minato et al., 1984).

The following are the in situ exchangeable cations, mean (Standard Deviation), for zeolitic samples from Escott, the main unit at The Gap, and the minor zeolite unit B at The Gap:

	Na	K	Ca	Mg	Total
Escott (AEC>70, n=14)	10(8)	12(8)	64(7)	13(3)	100(10)
The Gap (AEC>70, n=9)	19(18)	14(12)	49(10)	6(2)	87(21)
The Gap Unit B (AEC>70, n=3)	44(6)	3(2)	42(20)	8(3)	96(21)

The above are the mean (standard deviation) meq/100 g of cations released from the natural zeolite after exchange with ammonium acetate in the first part of the Standard AEC determination (Fredrickson, 1986).

The mean values above are plotted on the (Ca+Mg)-Na-K tertiary plot (Fig. 6) and can be compared with the whole rock and zeolite crystal cation ratios. The exchangeable cations position on the (Ca+Mg)-Na side relative to the respective whole rock assays confirm that potassium is retained within the rock, probably in orthoclase crystals, and not exchanged. This can be compared with the zeolite crystals (data only available from Escott) which shows approximately equal Na and K are exchanged out, combined with a larger proportion of Ca+Mg.

XRD STUDIES

Early X-ray powder diffraction (XRD) studies on the samples from Escott showed the zeolite became X-ray amorphous near 400°C, which was interpreted according to the paper by Mumpton (1960), to imply heulandite. This, combined with the high divalent cation content, resulted in the previously published papers on Escott mineralogy (Flood, 1991; Flood & Taylor, 1991; Flood et al., 1993) to specify heulandite.

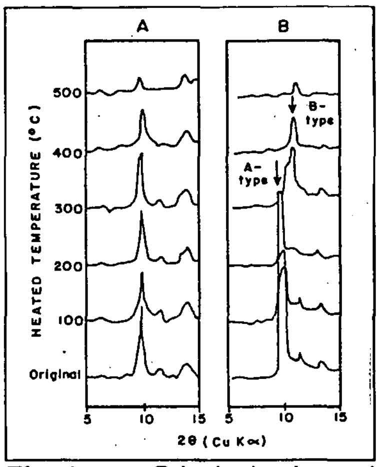


Fig. 10 Principal thermal XRD difference between Ca-clinoptilolite (**A**) and heulandite (**B**). Adapted from Minato & Namba, 1984.

Early this year further thermal XRF work was completed by H. Minato (University of Tokyo), based on the study of Minato et al. (1984). This requires subjecting a powdered sample to an elevated temperature for 4 hours, followed by XRD. This is repeated with duplicate samples and increasing temperatures, generally in 100°C steps. The resulting curves show the transition to B-type heulandite if heulandites are present (Fig. 10), and is considered diagnostic by Minato & Namba (1984).

The resultant XRD patterns are shown in Figure 11 for Escott. Note the peak at 9.6 does not shift to the right on the 300°C curve indicating no B-type Heulandite, and it finally diminishes

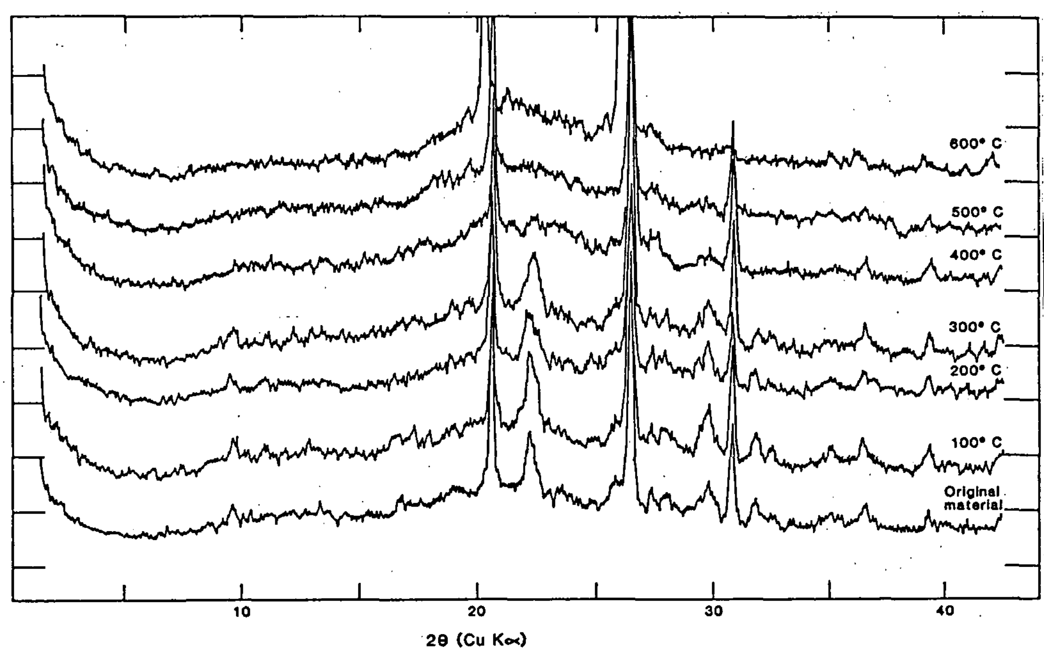
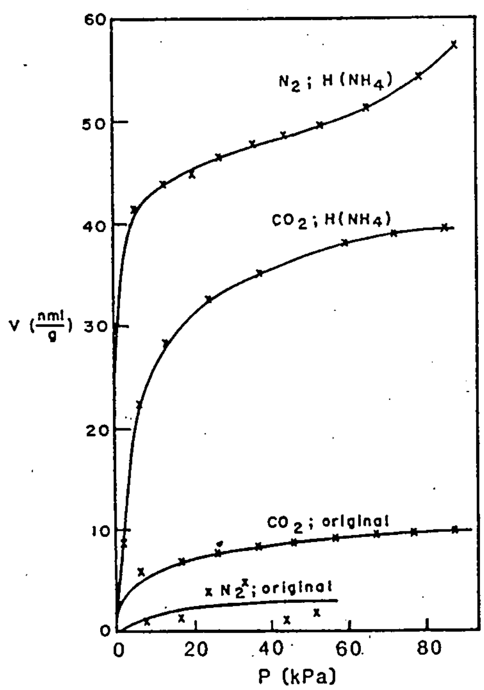


Fig. 11 Different XRF patterns by heating powder sample from Escott.
Analysis courtesy of Prof. Hideo Minato, University of Tokyo.

near, and is just visible at 400°C, thus indicating the sample contains Ca-clinoptilolite. The main peak at 22.4 as expected for Ca-clinoptilolite also becomes subdued by 400°C.

ADSORPTION MEASUREMENTS

The dehydration properties of zeolites are important in evaluating adsorbent applications. Thermogravimetric (TG) and Differential Thermogravimetric (DTG) analysis have been completed on an Escott sample by H. Minato (unpublished data, Tokyo University). The resultant curves (Fig. 12) resemble those provided by Gottardi & Galli (1985) for clinoptilolite, and does not show the prominent sharp TDG peak at 280°C resulting from the inversion to heulandite B. The Escott thermal curves show one continuous water loss from 50°C, but there are minor aberrations at 170°C and at 320°C reflecting the high calcium content of the clinoptilolite (Gottardi & Galli, 1985), and corresponds to thermal behaviour type 2.



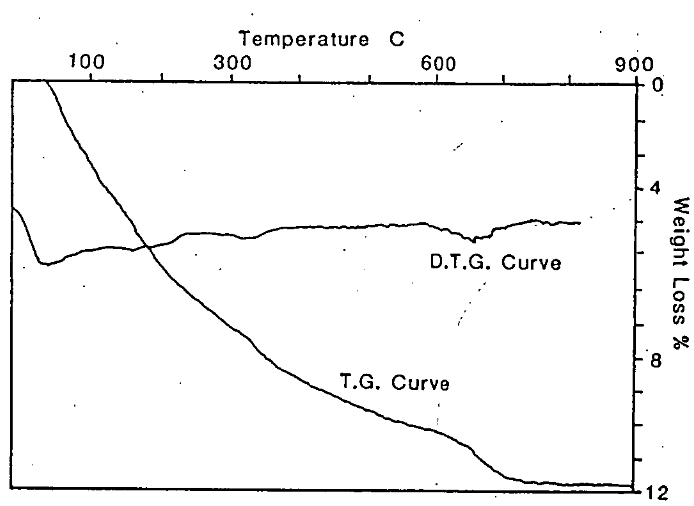


Fig. 12 N_2 and CO_2 adsorption and thermogravimetric curves for Escott Natural Zeolite.

Provided also (Fig. 12) are CO_2 and N_2 adsorption capacity curves for Escott Natural Zeolite. They show, as expected by the study of Yucel & Culfaz (1988), greatly decreased capacity of the Ca rich clinoptilolite, relative to the NH_4 exchanged form of clinoptilolite.

The adsorption of N_2 is related to the surface area of the zeolite. Due to the compact nature of the rock, (i.e. grain density virtually equals rock solid bulk density) the natural Ca form gave no useful results. But after exchange with NH_4^+, and subsequent deammoniation by heating to

350°C, the adsorption increased dramatically, with an estimated area of 190 m^2/g (J. Papp & D. Kallo, personal communication). This compares with an internal specific surface of 300 to 600 m^2/g for Hungarian 'Hydrolite' clinoptilolite (unpublished data sheet by Hydro-Trade, Hungary).

SOLID STATE NMR

The nature of the water within the Escott Mine zeolite material was also investigated by solid state Nuclear Magnetic Resonance (NMR) carried out by the CSIRO Division of Materials Science and Technology (Clayton, Victoria). Following the investigation by Ward & McKague

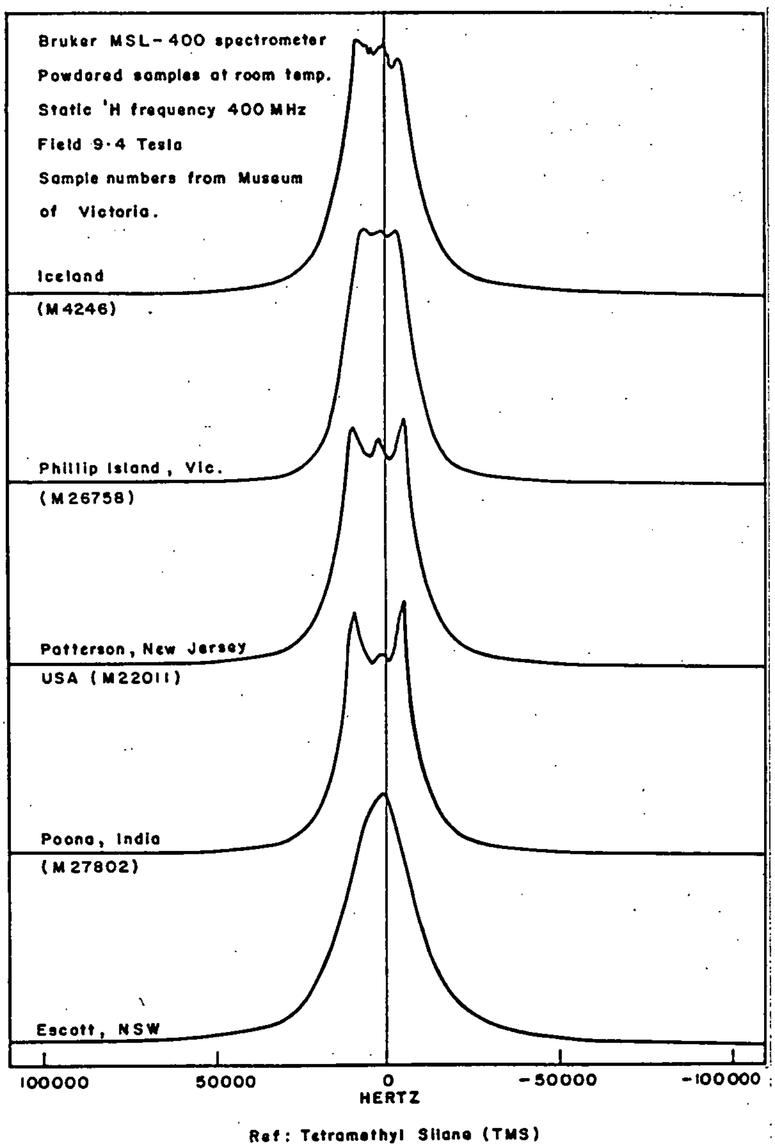


Fig. 13. Static proton NMR wideline spectrum for four samples of heulandite, and one sample of clinoptilolite (Escott).

(1993), heulandite at room temperature is expected to exhibit a classical Pake doublet pattern, in contrast to a Gaussian shaped curve for clinoptilolite. The Gaussian curve is indicative of randomly dispersed water molecules, whereas the Pake doublet pattern is indicative of more rigid localised water (Pake, 1948). Thus the water in heulandite is more ordered than clinoptilolite, until above 175°C when the transformation to Heulandite B (Boles, 1972) results in water similar to clinoptilolite (Ward & McKague, 1993).

A sample of Escott regular powder (ground to -100 µm) with no pre-heating, was examined using the CSIRO's Bruker MSL-400 solid state NMR spectrometer. The resultant curve (Fig. 13) showed a near Gaussian distribution. As a comparison, samples of crystalline heulandite obtained from Poona, India; Patterson, New Jersey; Phillip Island, Victoria, and unspecified location from Iceland, were examined after powdering. As expected from Ward & McKague (1993), the heulandite samples displayed a Pake doublet pattern indicative of hindered rotating water.

All four heulandites, but more pronounced with the Paterson and Phillip Island samples, displayed a third middle peak. This is possibly reflecting a portion (relative to the area under the curve, about 5%) of the sample having more random hydroxyls. A possible further consideration which still needs to be resolved is the effect of iron oxides and clays (Dr. T. Bastow, personal communication), which are present in most zeolite bearing rocks (around 1% total Fe and 5% clay minerals in Escott), compared to the relative pure crystal samples of heulandite tested.

This study seems to confirm the observation made by Ward & McKague (1993) regarding the proton NMR static wideline spectrums for clinoptilolite and heulandite. This method has potential to provide a cost effective (compared with thermal XRD) method of distinguishing the two separate minerals. Further work using this technology could involve the study of the dehydration of the zeolites providing information on the structural frameworks (as outlined by Ward & McKague). Another avenue of study is to also test the zeolite structure after major cation exchanges.

PHYSICAL PROPERTIES

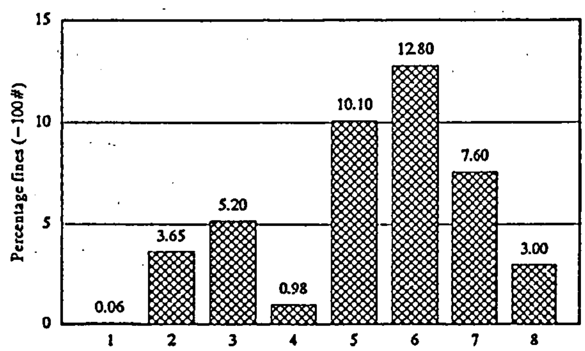
One of the distinct differences between Australian Carboniferous zeolitic rocks, and most zeolitic rocks mined overseas, is the physical appearance relating to its whole rock density and hardness. The Brinell hardness test performed on a sample from Escott and The Gap both gave approximate measurements of 30. This is comparable with quartz cemented sandstone (ranges

25 to 40, ACS Laboratories Pty Ltd, 1993). In contrast a sample of white Indonesian zeolitic rock from Java completely failed the test.

The results of density measurements are also just as different, as is illustrated with the following density data:

	Bulk Solid Density	**Apparent Crystal Density**
Escott Mine Site	2.23	2.23
The Gap (G300)	2.32	2.33
Indonesian (Java)	1.41	2.20

The similar apparent grain density reflects the mineralogy of the sample. All samples are composed of similar minerals with comparable densities, the Indonesian containing slightly less amounts of denser quartz and feldspars gangue. The bulk rock density was determined from the measured porosity (by Helium injection) and apparent crystal density (from porosity and volume determined by mercury immersion). The closeness of the Werris Creek bulk and crystal densities reflects the 'tight' interlocking nature of these samples, reflected in the high resistance to deformation as tested by the Brinell hardness test. The solid rock density of the Java Indonesian sample (typical of most Recent overseas zeolitic rocks) reflects the open nature of the constituent crystal grains, but owing to weakly cemented grains fails the Brinell test.



1. Commercial pool sand filter. Clinoptilolite rocks from 2. Akvaro-Sorb, Hungarian, 3. Java Indonesian, 4. Escott, N.S.W., 5. Hector, U.S.A. & 6. New Mexico, U.S.A. Also synthetic 7. Linde AW-500 chabazite, & 8. Zeolon mordenite. Samples 5 to 8 from Mercer & Ames, 1978.

Fig. 14 Wet Attrition Test results for synthetic and natural zeolites, and for a normal pool filter sand.

Another physical property currently being measured is the Wet Attrition Test by Mercer & Ames (1978) which evaluates the zeolites ability to withstand repeated hydraulic lifting during backwashing in zeolite columns or beds. This test is required by those evaluating zeolite ion exchange columns. The results to date indicate that Escott zeolite is far superior in withstanding attrition compared to overseas natural and synthetic zeolites (Fig. 14). Resistance to attrition is also important in turf applications.

ZEOLITE FORMATION

Zeolites can form in a wide range of geological environments including crystallisation from hydrothermal fluids, contact or low grade burial regional metamorphism, alteration of volcanic materials in closed saline-lake systems, alkaline soils, or open freshwater-lake or groundwater systems, and deep marine settings. The exact mechanisms of formation are not well understood, but zeolites in the sedimentary rocks probably formed by dissolution-reprecipitation reactions (Mumpton, 1978).

The Ca-clinoptilolite within the Tamworth Belt and the Drummond Basin has all formed in waterlain rhyolite tephra under non-marine, open hydrological conditions, in contrast to the closed systems (Surdam, 1977) present in saline alkaline lakes like the current Central Australian lakes. This is shown by the zeolitisation crossing lithological boundaries, both vertically and laterally. Which units are altered is constrained by the amount and activation of silica available (i.e. the lithic sandstones are only weakly zeolitic), or by sufficient initial porosity for water saturation (i.e. the welded ignimbrite below the main Gap unit not zeolitised).

The expected vertical zonation for open systems (Hay, 1978) is not shown due to the relatively thin units suitable for hydrolysis and solution of silicic glass to form zeolites, also the zeolitic units are separated by relatively impervious units (welded ignimbrites). In comparison the vertical zonation is observed over a 1.8 kilometre thick sequence of zeolitic Tertiary tuff at the Nevada Test Site (Sheppard, 1973). The two previous published papers on the Escott mineralogy, Flood (1991), and Flood & Taylor (1991), also discussed the formation within an open system.

There appears to be an imprint of burial metamorphism on the Tamworth Belt zeolite units, as indicated by the prevalence of clinoptilolite and mordenite in the top of the sequence, and laumontite content increase towards the base (New South Wales Dept. of Mineral Resources, 1986b).. Zeolite formation, in particular sediments containing volcanic debris, generally favour the formation of clinoptilolite (Gottardi & Galli, 1985), and the clinoptilolite-heulandite group can be formed at temperatures as low as 65°C in areas of silica saturation (Kristmannsdottir & Tomasson, 1978). It is concluded that the zeolite formation within the Currabubula Formation was by zeolite crystallisation at the expense of dissolving volcanic glass (Hay, 1978; Gottardi & Galli, 1985) within a open hydrological system to begin with, and continued to develop as the sediments were buried. Zeolitised units were dependent on silicic content, combined with porosity and availability of water (the deposits all appear to be originally topographic lows).

ESCOTT RESERVES AND MINING

The composite unit mined at Escott has a proven reserve based on drilling, costeaning, and mapping of 132,000 tonnes, down to 15 metres depth, with minimum grade of 120 meq/100 g. There is a probable 50,000 additional tonnes along strike that have not been drill tested. The units have been shown by the RC drilling to extend down at least to 30 metres, but this extra depth is not being considered currently due to the excessive waste to ore ratio (2:1) required for extraction. It is planned to complete a more detailed pit optimisation assessment to possibly economically recover this deeper material. There is an extension along strike (Fig. 3) of the zeolite units within the Mining Lease Application, but these have not been systematically tested to date.

2.3 THE GAP PROJECT, NEW SOUTH WALES

The Gap location is due west from the town of Werris Creek, and 4 kilometres north-north-west from the Escott deposit. The unit under consideration for mining is greater than 35 metres thick and dips 28° to the east (Fig. 15). It has an unconformable top, and a concealed basal contact. The entire unit is massive and lacks any macroscopic texture, except a brecciaed appearance. It appears as a massive red devitrified pumiceous unit, lensing and thinning away from the proposed mine site. This site contains a significant zeolite resource, but due to environmental factors the decision to develop is still under consideration.

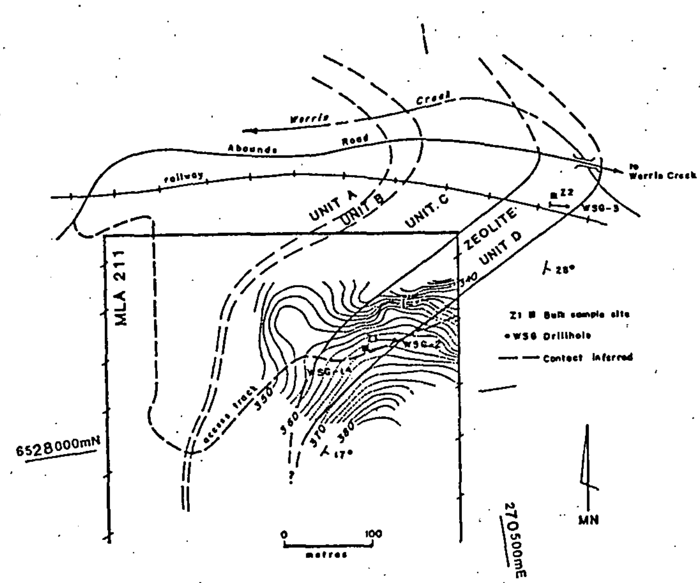


Fig. 15. Geological sketch map of The Gap location. The surveyed topographic contours show the steep slope down to the railway line below.

STRATIGRAPHY

The basal unit in the outcrop area is a purple polymict orthoconglomerate (Unit A, from Flood, 1987). This is overlain by a dark red-purple zeolitic vitric pumiceous tuff (Unit B) exposed near the creek, but not well exposed elsewhere.

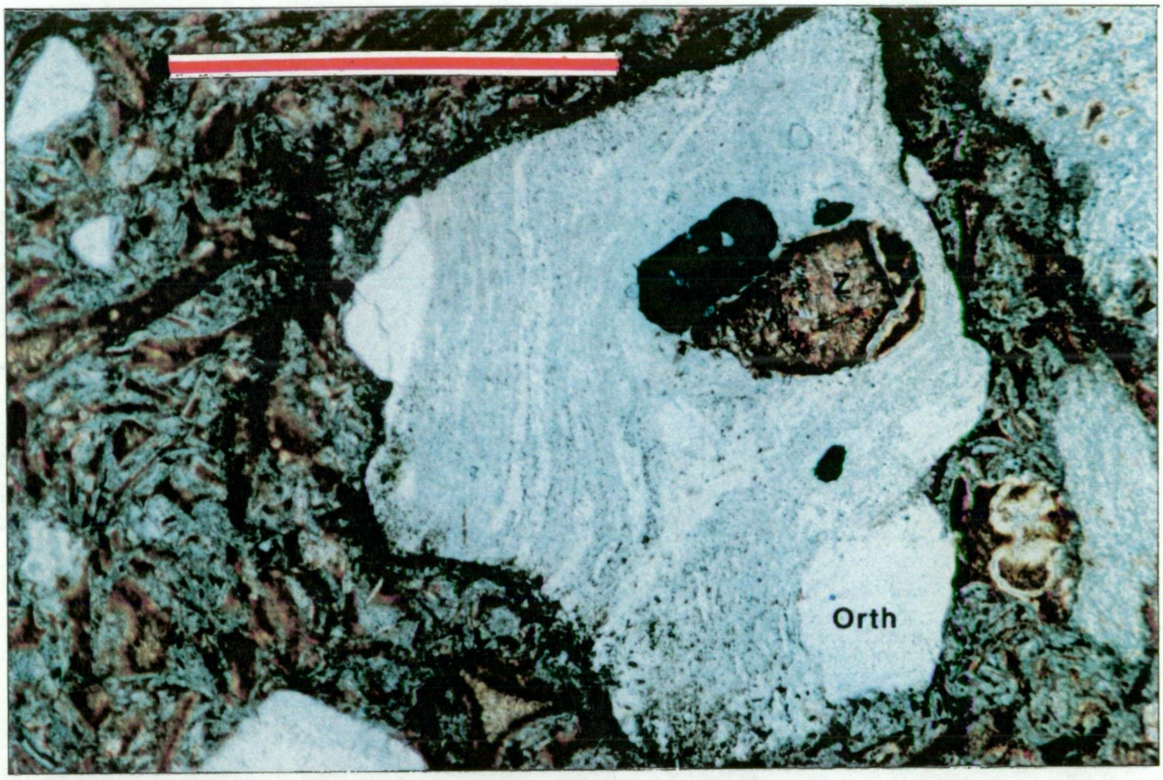
The next unit is a welded ignimbrite (Unit C) below the main zeolitic unit. It is about 15 metres thick, pale pink to cream and composed of approximately 75 percent glass shards, 20 percent phenocrysts, and 2 percent opaques. Most of the phenocrysts are extensively altered plagioclase crystals showing major resorption and sericitisation. Smaller anhedral quartz grains are present. Towards the top alteration is more intense, plagioclase is reduced to skeletal grains, and the groundmass shows extensive fine grained sericite alteration. There are also minor lithic fragments containing glass shard textures. It is not certain that this is one complete unit, due to the lack of continuous outcrop. The groundmass does not show zeolite alteration as confirmed by low AEC measurements (11 meq/100 g).

The main zeolite body, and that being examined for mining, is Unit D, about 35 metres thick. It is a pink light red lithic vitric pumiceous mass flow deposit. Minerals present include angular phenocrysts of plagioclase, albite and oligoclase, that are undergoing alteration to biotite and sericitic micas. Orthoclase occurs as rounded euhedral crystals resulting from resorption. Clasts of other pyroclastic rocks are present, often showing flow textures (Fig. 16) and containing feldspars phenocrysts. Zeolite minerals are restricted to the matrix, specifically in the alteration of the glass shards which are very abundant.

The geometry of the base is not visible due to scree, but the boundary is tentatively picked from aerial photographs and ground mapping. The unit appears to be a lens shaped body, the thickest part outcropping up the side of the hill.

Overlying the main zeolite unit is a distinctive light emerald-green coloured welded volcaniclastic sandstone (Unit E, Fig. 16) about three metres thick, that is black when fresh. This unit contains 50-60 percent phenocrysts composed of older ignimbritic slice fragments, phenocrysts of fragmented plagioclase, mainly andesine with altered cores and resorbed rims, sericite altered orthoclase anhedral phenocrysts, minor biotite, in a matrix of fine grained chloritic minerals. Celadonite has also been observed in the altered groundmass.

Overlying the green unit is a crystal rich ignimbrite dominated by plagioclase phenocrysts. This in turn underlies a series of thinly bedded pale brown welded ignimbrites and volcaniclastic sandstones. The welded glass shard matrix of the ignimbrites are slightly devitrified with minor zeolite and clay minerals nucleating. This sequence then appears to be covered by typical fluviatile conglomerates and sandstones of the Currabubula Formation.



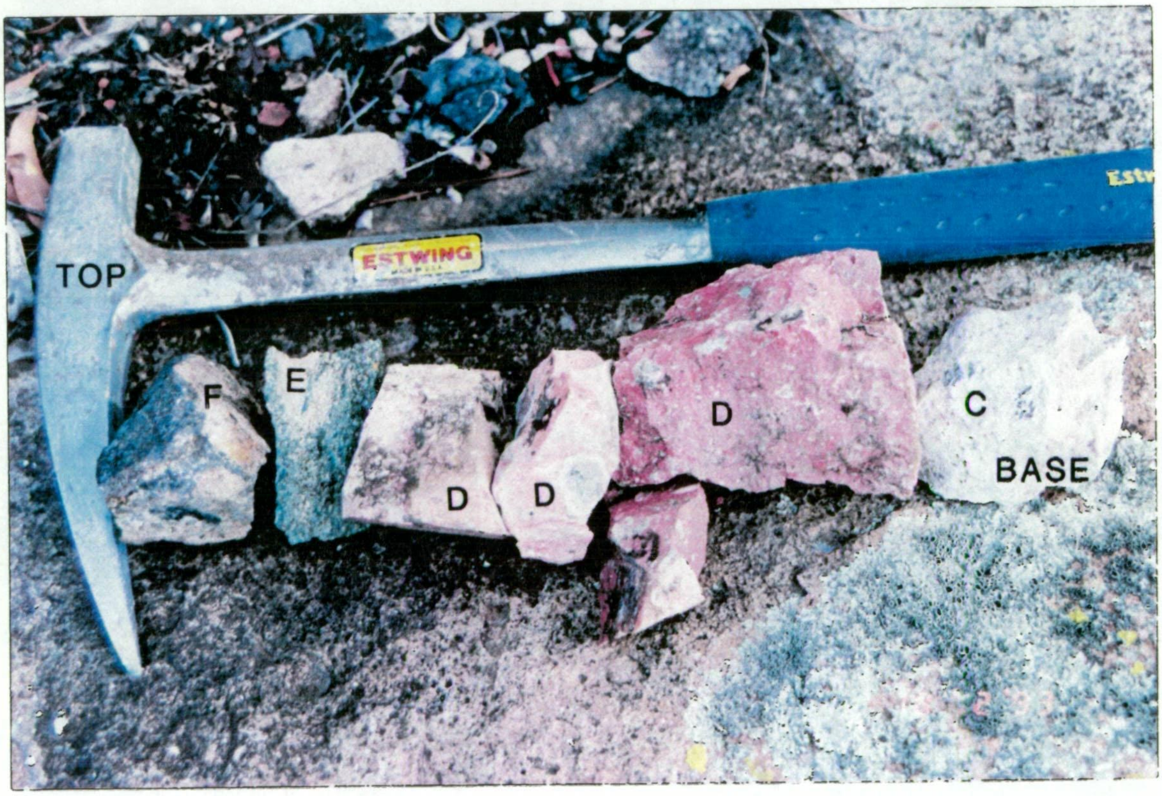


Fig. 16 TOP: Thin section of sample from near the base of the main zeolite unit (D) at The Gap showing typical clast and shards. Scale bar 1 mm. BOTTOM: Samples across the sequence at The Gap.

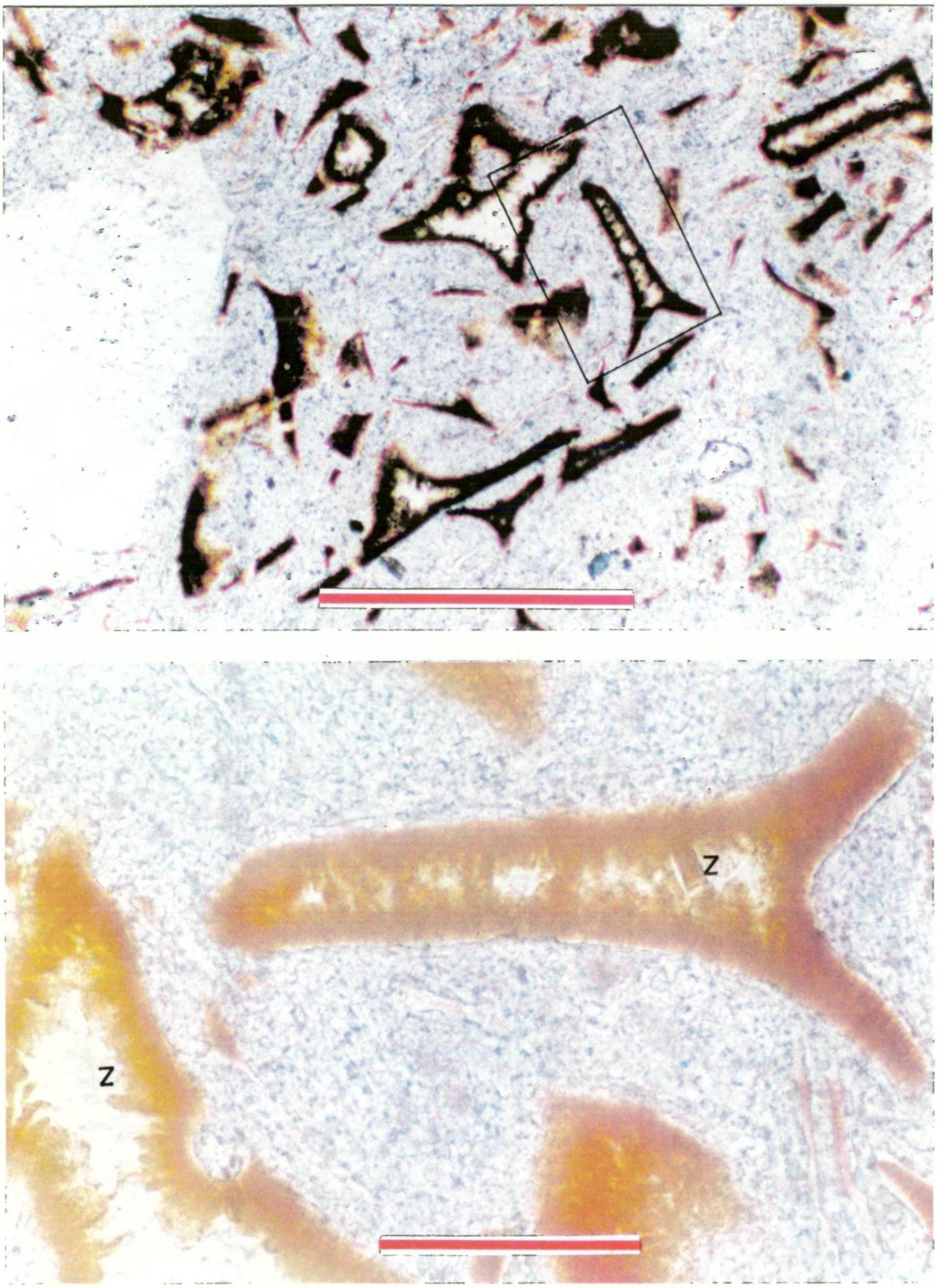


Fig. 17 TOP: Sample (G260) from The Gap, near the top of unit D, showing glass shards. Scale bar 0.5 mm. BOTTOM: Enlargement of top photograph showing Ca-clinoptilolite crystals growing into, and replacing, the glass shards. Scale bar 0.1 mm.

RESERVES AND MINING

The recoverable reserves, based on the drilling and mapping, indicate that possibly 50,000 tonnes should be recoverable from The Gap Mining Lease Application. This is far less than the 250,000 tonnes indicated resource reported in 1987 (Pecover, 1987) due mainly to the difficulties of mining without risking the railway line below the main exposure. Currently, different open pit designs are being considered, and the decision to mine has not been finalised.

2.4 CURRABUBULA (SHEEDY) PROJECT, NEW SOTH WALES

The Currabubula Zeolite Project (also called Sheedy's or Kappmm area) deposit is located near Spring Creek, west of the town of Currabubula. It was first isolated when rockchip samples returned very high AEC values. Subsequent drilling (Cooper, 1992) confirmed the grade and thickness of two units. The vitric, non-welded, zeolitic tuff units, up to five metres true thickness, with at least five individual units, outcrop within a 750 metre thick sequence of terrestrial conglomerates and sandstones. Due to thickness limitations, only two of these units are planned for mining. The main unit is laterally continuous for over 3 kilometres and is overlain by conglomerates. The units are near the northern end of the synclinal axis, on the west limb dipping 30° east, striking north south.

The units are non-welded vitric ignimbrite showing 80 to 90 per cent groundmass with the remaining crystal phenocrysts and occasional lithic fragments. The phenocrysts are hornblende and resorbed biotite as the major phase, followed by orthoclase and plagioclase sparsely in the rock. In section the dominant feature is the glass shards occurring interstitially between the phenocrysts. There is occasional zonation in which areas are richer in glass shards, together with fine aggregates of plagioclase that may reflect blobs of crystallising flow. In a sample collected further to the south, schistose clasts, together with sedimentary inherited quartz clasts occur within bands (B. Mapanu, 1993, personal communication).

The units are enclosed within a sequence of pebble conglomerates grading upward into siltstone and fine sandstones. These are interpreted to be fluvial grading up to lacustrine facies. There is local minor lateral strike faults, which generally are preferred locations for current drainage.

SEM images have confirmed that the zeolite occurs as thin plate crystals of clinoptilolite showing no preferred orientation. While the natural exchangeable cations have not been measured, calcium, followed by potassium are the likely cations based on the whole rock chemistry (Appendix 1).

RESERVES AND MINING

Following percussion drilling and surface mapping, the opencut reserves are 280,000 tonnes at 135 meq/100 g indicated, with another 250,000 tonnes inferred by surface mapping (Fig. 18). This opencut tonnage would have a waste to ore ratio of 1.4:1 and a maximum depth of 13 metres. Given the market conditions, a single bench pit following the strike, with a lower waste to ore ratio will be commissioned initially.

Some of the highest AECs in Australia with values of 146 meq/100 g over 4.3 metres have been recorded from the main zeolite unit within the two adjacent Mining Lease Applications (MLA 261 & 262).

2.5 WILLOWS PROSPECT, QUEENSLAND

This potential zeolite mining area is within the Drummond Zeolite Province, in the area south west of the township of Anakie. Incomplete reconnaissance has delineated several zeolite units within the Ducabrook Formation which were known to contain numerous tuffs (Pinchin, 1978). This Formation is near the top of the Drummond Basin sequence. Outcrop is restricted to creek and road cuttings, due to overlying gravels (mined locally for sapphire) and very shallow dips. Problems with lack of outcrop result in correlation difficulties.

The area is within the Scholfield Syncline, with a gentle fold axis running northeast, plunging to the south. Generally the altered tuff and tephra are relative flat lying units interbedded with felspathic-lithic sandstones and green mudstones of the Ducabrook Formation (Harms, 1990) representing fluvial and lacustrine environments. Plots of Zr/Ti-Nb/Y (Fig. 9) confirms the rhyolitic nature of the original rock source. While generally the zeolite units are red to pink, at least one unit is white in colour. Detail on the individual units is restricted to very preliminary descriptions provided by Harms (1990) who has conducted reconnaissance mapping and sampling. Figure 19 shows one typical location, along the Highway, where the 2.4 metres true thick composite unit returned AEC of 91 meq/100 g (sample QZ40). This site shows the lack of prominent outcrop for these units, and would not have been visible without the road cutting.

Recent thin section examinations and microprobe analysis (sample W2) by P. Flood (personal communication) on samples from the Willows area showed similarity to Escott in that they are generally either fine-grained, red to pink pyroclastic or laminated silicic mudstones and siltstones. The units show well preserved vitroclastic texture and the glass shards are now altered to Ca-clinoptilolite. Early XRD and SEM work by Zeolite Australia confirmed the zeolite mineralogy as

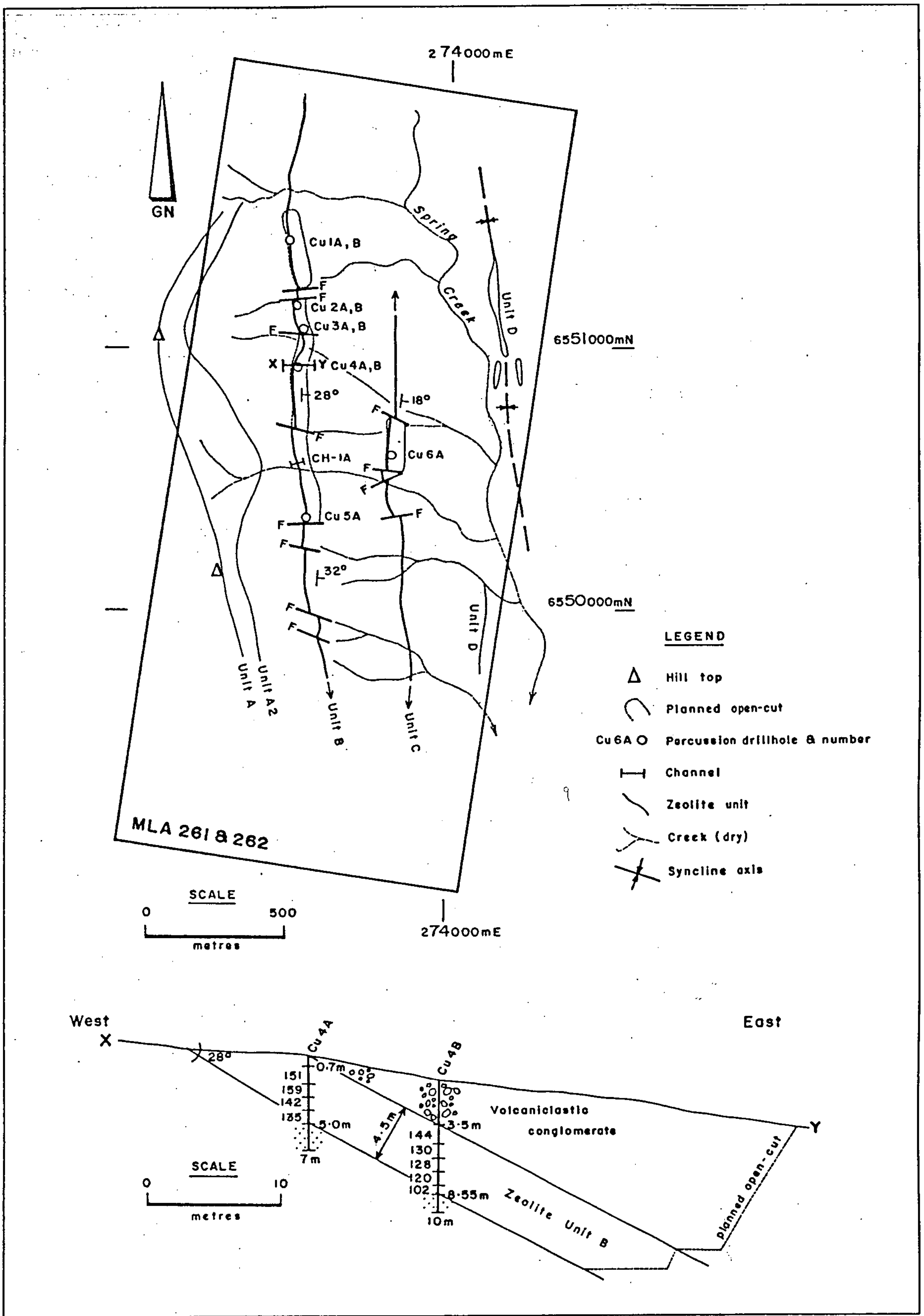


Fig. 18 Zeolitised units within the Currabubula Mining Lease Application area, together with cross section showing AEC values (meq/100 g) obtained from air track holes.

Fig. 19 Example of pink zeolitic unit, 2.4 meters thick, exposed along the Capricorn Highway, west of Willows Gemfield turn off. Internal bedding structure is visible (photo from Harms, 1990).

consisting of platey crystals of similar habit to Escott. While CEC has not been determined, from the whole rock analysis it can be expected that the Drummond Basin clinoptilolites are Ca based. This has been confirmed by P. Flood, as his work shows the Drummond Basin samples become amorphous above 400 °C as expected for Ca-clinoptilolite. Microprobe work shows the Drummond Basin shards are similar to Escott, with the altered shards richer in calcium than the groundmass, but here they also show more potassium. Whole rock chemistry, together with the microprobe analysis are provided in Appendix 4 and 5.

RESERVES AND ECONOMIC POTENTIAL

The AEC values to date, confirmed by petrological and chemical analysis, suggest that the zeolitic beds are suitable chemically for development. Further work requires drilling and delineation of the reserves before the economic potential can be given with confidence. The area is close to a major highway, and railway line which head towards the large horticultural area of central coastal Queensland. This economic factor will determine, once geological considerations have been met, whether development will continue.

3. EXPLORATION AND MINING

Economic exploitation of zeolites in Australia is currently active only in New South Wales, with mining occurring at one site, and proposed at a further two sites.

3.1 AUSTRALIAN ZEOLITE EXPLORATION HISTORY

Bramlette & Posnjak (1933) over sixty years ago observed that clinoptilolite is a very common and intense alteration products of pyroclastics in a study of Californian Miocene pyroclastics.

Scientific reports on Australian authigenic zeolites commenced with Coombs (1958) reporting the complete zeolitisation of tuffs near Seaham, N.S.W. The occurrence of zeolitic pyroclastic tuffs within the Currabubula Formation was noted by Wilkinson & Whetten (1964), with Whetten (1965) further recording the extensive development of zeolites, including analcime, heulandite, clinoptilolite, and laumonite within the tuffs and volcaniclastic rocks from the Werrie Basin. This was followed by Loughnan (1966) with the report of up to 35 percent analcite within thin (15 cm), silica rich tuffaceous units in the Permian Newcastle Coal Measures. At the same time McKelvey (1966) in his Ph.D. thesis thoroughly documented both clinoptilolite and laumontite within a 2000 metre stratigraphic section of the Rocky Creek Syncline, outlining both diagenetic and burial zeolitisation.

In 1973, MacNevin completed probably the first economic review of known Australian zeolite occurrences, with brief descriptions of zeolitic rich rocks in New South Wales. An early attempt at obtaining an economic resource of Australian zeolites was made by beneficiation of zeolites from basalt breccia voids in Tasmania, but this was abandoned due to the perceived prohibitive cost of crushing and processing (Askins, 1980).

The belt extending from Tamworth to Newcastle was considered to contain significant occurrences of natural zeolites (Holmes, Lismund, & Oaks, 1982), and considerable potential was given for discovery of an economic deposit according to the State Government Geological Survey. Following up on this opinion, the N.S.W. Department of Mineral Resources commenced the Zeolite Project in 1985. By the end of 1987, the Department had sampled and investigated extensively across eastern New South Wales and had confirmed the existence of potentially economic reserves of natural zeolite. In conjunction, research students from the University of New England also assisted in delineating potential zeolite outcrops, primarily around the northern Tamworth Belt.

An important phase of company exploration followed the Zeolite Project initiated by the N.S.W. Department of Mineral resources with exploration companies actively searching for authigenic sedimentary zeolite deposits. Exploration Licences were granted to JM Stephen Pty Ltd in early 1987 over large delineated areas. In late 1987 a Joint Venture agreement was drawn up between JM Stephen and Mount Gipps Limited, a public mining company, to develop the zeolite Licences. In December 1987, zeolite mining began, followed in middle 1988 with the first commercial sales by the Joint Venture of Escott Natural Zeolite.

The Department of Mineral Resources Zeolite Project concluded with the issue of an Information Package for Exploration and Development of Natural Zeolite (Holmes & Pecover, 1987) and the Proceedings of a Seminar on Zeolites in New South Wales (NSW Department of Mineral Resources, 1987) designed to initiate commercial interest in exploration and mining for natural zeolites.

Other companies also followed the initiative in NSW and conducted exploration, but most have fallen by the way due to either lack of suitable material, lack of institutional funding support, or lack of experience with marketing zeolites. Many were small companies which quickly obtained areas with outcropping zeolitic rocks, but then became disillusioned when no markets suddenly appeared for their product. An example is International Mining Corporation NL which drilled and collected small bulk samples (Hawley, 1991) and even publicly reported large tonnages (Roskill Information Services Ltd, 1990), but finally abandoned the area due to reported lack of market development. Later review has also shown that the 'tonnage' was inferred and not amenable to low cost mining and thus the deposit would not have lived up to the market's perception.

Currently in Australia, only one company, Zeolite Australia Limited, is producing zeolite from a small single open cut mine (Escott). A handful of other companies still hold title over ground prospective for zeolites, including Centenary International Mining Ltd and Commercial Minerals Limited.

3.2 EXPLORATION TECHNIQUES AND RATIONALE

Zeolite exploration in Australia began when the N.S.W. Department of Mineral Resources commenced their Zeolite Project aimed at investigating and encouraging the development of zeolite mining within the State. Following literature reviews, the Department conducted a wide ranging rock chip sampling program over any known or potential areas based on regional mapping. Close to one thousand samples were collected and examined, but the most useful information has been the development of standard laboratory techniques and characterisation of the Australian zeolite rocks recovered. This included comparing these same laboratory techniques on overseas zeolite samples.

This time consuming and expensive laboratory work would have been extremely difficult for a mining company to undertake as it needed to be completed, even before a economic site could be proven to exist in Australia. The N.S.W. Department must be commended for providing such incentive to private mining companies.

3.3 FIELD METHODS

It is recognised that subduction related (as can be seen from the Winchester & Floyd plot) volcanic arcs on continental margins are required, and as outlined by Flood (1991), the flanks adjacent to these ignimbritic centres form the most prospective zone for zeolite exploration. Within this zone large lacustrine, or water saturated environments containing silicic tephra are prime sites for inspection.

Initial exploration indicated that significant zeolitic mineralisation is constrained to tephra lithologies. Features considered useful as an indicator of suitable volcaniclastic beds included the following field descriptions;

1. Persistent outcrop along strike, reflecting the strong cementation of the zeolitised units,
2. Little vegetation other than lichens growing over outcrop.
3. Conchoidal fracture, easily shattering and breaking with sharp edges,
4. Vitric lustre.
5. Red to pinkish colour, not always present and may be green. In Queensland a white zeolite bed has been sampled.

Not all of these features are visible in any one outcrop.

While field testing kits for zeolite exploration have been advocated (e.g. Hellferich, 1964; NSW Department of Mineral Resource, 1986a), these have not been utilised mainly due to the problems in organising the necessary chemicals. This opinion was also expressed with "... it is better suited to the laboratory than the field" by Sheppard (1973, page 692).

Generally rockchip or channel samples are collected during reconnaissance mapping. The first test is to determine the Standard AEC. If this is positive (>70 meq/100g) then the sample is petrologically and XRD examined, and if the presence of zeolites is confirmed, then whole rock assay may be completed. Generally with this information, a site can be considered potential, and worthy of more detailed mapping, sampling, and depending on continuing positive results, RAB drilling to confirm thickness and vertical grade. RAB drilling has proved effective and cheap. While tonnage is not a problem with massive zeolite deposits, the availability of close markets, or competitive freight is more influential in deciding if a site can be developed.

The cost per sample for Ammonium Exchange Capacity is approximately $30/sample, minimum six samples per batch. The determination of exchangeable cations is more expensive. But for a first pass approximation it is possible to determine the amount of individual cations exchanged from the natural state by comparing the whole rock geochemistry of the sample. Using the AEC as a measure of the total potential exchange, then the ratio can be determined from the whole rock assay.

3.4 MINING AND PRODUCTION

Fig. 20 Looking south, along strike, into the Escott Zeolite Mine, Werris Creek. Photograph taken February 1993 when pit was approximately 50 metres long.

National zeolite mining in Australia is restricted to the Escott Zeolite Mine (Fig. 20), 5.5 kilometres south west of the rural township of Werris Creek. The zeolite is currently mined on a regular basis from the Escott site by conventional open cut methods (Marx et al., 1993). All mining and transportation from Escott mine site to processing facilities has been by local contractors as required. Airtrack drilling and blasting using nitropril and electric detonators is used to blast up to 1500 tonne shots.

Grade control is conducted using face channel sampling, together with the results of the detailed exploration drilling. As the zeolite units mined can be visibly distinguished, the sampling serves to confirm overall grade. Lower grade but still zeolitic units occur in the hanging and footwalls.

The broken ore is loaded by excavator onto trucks which carry it some 240 kilometres south to Mudgee on a campaign basis, where it is crushed and screened to produce various sizing's. Other processing plants in Melbourne, Newcastle, and Sydney, have also been utilised when necessary. During 1993 a screening plant was installed by Zeolite Australia to offer the company greater ability to economically produce new sizing's for market development.

The raw run-of-mine material is crushed in a primary jaw crusher to yield minus 50 mm product, followed by a secondary gyratory crusher producing minus 6 mm chips. This is the feed for the screening plant, or if powder is required, it is fed into a Bradley, vertical-shaft roller-mill. Storage space at the custom milling operation is limited to approximately 100 tonnes with a further 50 tonne warehouse in Melbourne.

Current operations produce zeolite in the sizes -6.0+2.0 mm; -2+0.5 mm; -1.0 mm; -1.0+0.25 mm; minus 100 μm and minus 50 μm. These sizing's are in line with market requirements and are available in bulk, 1 tonne bulker bags, 40 kg and 20 kg plastic coated woven polypropylene bags and 20 kg double walled paper sacks on pallets. A range of retail packs are also available as 2 kg, 5 kg and 10 kg plastic bags. These products are different from those listed in Flood et al. (1993) and reflect the continuing adjustment of product specifications to meet market requirements. To date two grades have also been produced, the regular grade collected across strike, together with selective mining of premium grade material to meet individual clients requirements for a higher grade material.

All movements of zeolite material, whether internal transfers (mine to mill, mill to store etc), sales, or free of charge samples, are currently all databased using an in house developed program running under Microsoft Access. Due to the wide product range (sizing x package) and extensive range of market and clients, this program was required to keep track of sales and provide marketing information for categories based on zeolite application. The program also produces invoices, stock control statements, production statistics, and the statutory reports required by the Department of Mineral Resources.

Many of the smaller orders are of a trial or experimental nature resulting in frequent requests for different specifications. This results in difficulty in planning the upcoming production, often resulting in more expensive shorter production runs for many products. Accurate forecasting is essential in providing a "just in time" production system. New business from the expansion of markets also poses problems in this area as little notice is often given. This unavoidable inefficiency in production is similar to the problems faced by American Resources Corporation's zeolite deposit at Ash Meadows, California (Shelton, 1993).

GRADE CONTROL MEASURE

Grade or the measure of usefulness of zeolites is usually determined by the Cation Exchange Capacity (CEC) quoted in milliequivalents per 100 grams (meq/100 g). An equivalent is a measure of the relative ion concentration, and is the weight concentration divided by the equivalent weight (atomic weight divided by the valency) for that cation. The CEC is a measure of the number of cations per weight, or volume, available for exchange. Ammonium Exchange Capacity (AEC) is an approximation of CEC using ammonium as the measured exchanged cation. Unfortunately CEC is inherently difficult to replicate with natural zeolites, and this is compounded by lack of an Australian or International Standard for zeolite analysis. Numerous publications exist detailing the determination of CEC in zeolites including Busenbury and Clemency (1970), Mercer & Ames (1978), Noda (1979), Mian & Hilchie (1982), Semmens (1984), Ming & Dixon (1987), Lieu et al., (1988), Fredrickson & Dowswell (1988), Ming et al., (1991); together with many more dealing with CEC determination of soils.

The method adopted by Zeolite Australia Limited for measuring CEC and AEC is the batch method (described herein as the 'Standard' method) developed by the NSW Department of Mineral Resources (Fredrickson, 1986). While batch methods are not as effective as column methods for cation exchanges (Semmens, 1984), the Standard technique has been demonstrated to produce reproducible results from a wide range of physically different natural zeolites (Fredrickson & Dowswell, 1988) and confirms that strict control of sample preparation and exchange capacity test conditions is essential for precise and reproducible results.

Properties that influence the CEC and AEC readings include temperature (ions diffusion increases with temperature), particular saturation cations used (ion size, valency and hydration energy are important), cation concentration, exchange time (time is needed for ions to physically diffuse into the crystals), particle size (smaller particles have larger surface area and shorter diffusion paths), particular releasing cations used (related to selectivity coefficient of saturation cation), cation release and washing technique, and any previous pre-treatments (heating, acid washing, etc.). Figure 21 shows the differences caused by altering some variables on the Standard AEC of Fredrickson (1986). These variables lead to potential differences in exchange capacity determinations. A further example is soil CEC tests, with exchange times of only a couple hours, compared with the equilibration time for the zeolite analcime which can be as long as three days (Ames, 1966)

The Standard procedure provides an AEC, and if necessary can provide CEC of individual cations released. The procedure involves replacing the current exchangeable cations with NH_4^+ by treatment with 1M NH_4OAc for 18 hours, washing excess surface ammonium away, then replacing the exchanged NH_4^+ by treatment with 1M KCl for about 18 hours. The amount of NH_4^+ released is determined using an ion selective electrode, and the AEC calculated for the amount released by the 1 gram zeolite sample. The procedure takes three days, but batches of 24 samples are run concurrently, and is considered reasonably quick (Fredrickson & Dowswell, 1988). The cost per sample is approximately $30. The repeatability of AEC in high grade (>100) results is better than 8 meq/100 g, with precision decreasing as AEC increases.

If the exchangeable cations are required, the solution obtained from the initial NH_4OAc exchange is kept, and analysed for major cations. The sum of the cations released is equated to the CEC. If the CEC is higher than the measured AEC, then it is probably due to dissolving of salts (i.e. NaCl) raising the amount of measured cations released. Usually it is lower indicating that other cations not measured, usually Sr and Ba, are exchanged. The high presence of soluble salts is easily indicated by high conductivity and should be a regular test during initial exploration. The full CEC test is not done routinely due to cost, and the fact that whole rock analysis can provide a guide.

The AEC and CEC measured are not ***total*** cation exchange capacity, as is shown by the increases by heating etc, but will provide a close form of ***effective*** cation exchange capacity that enable comparison of relative exchange potential between zeolite samples. Most CEC tests are relative, and unless the similar techniques are employed by other laboratories, the CEC or AEC can not be compared closely. It is encouraged that zeolite application studies do at least one determination using the Standard test as outlined by Fredrickson (1986), combined with the effective (simulating the conditions to be encountered in practice, i.e. particle size, solutions etc.) CEC. This allows other researchers to determine whether the zeolite is comparable.

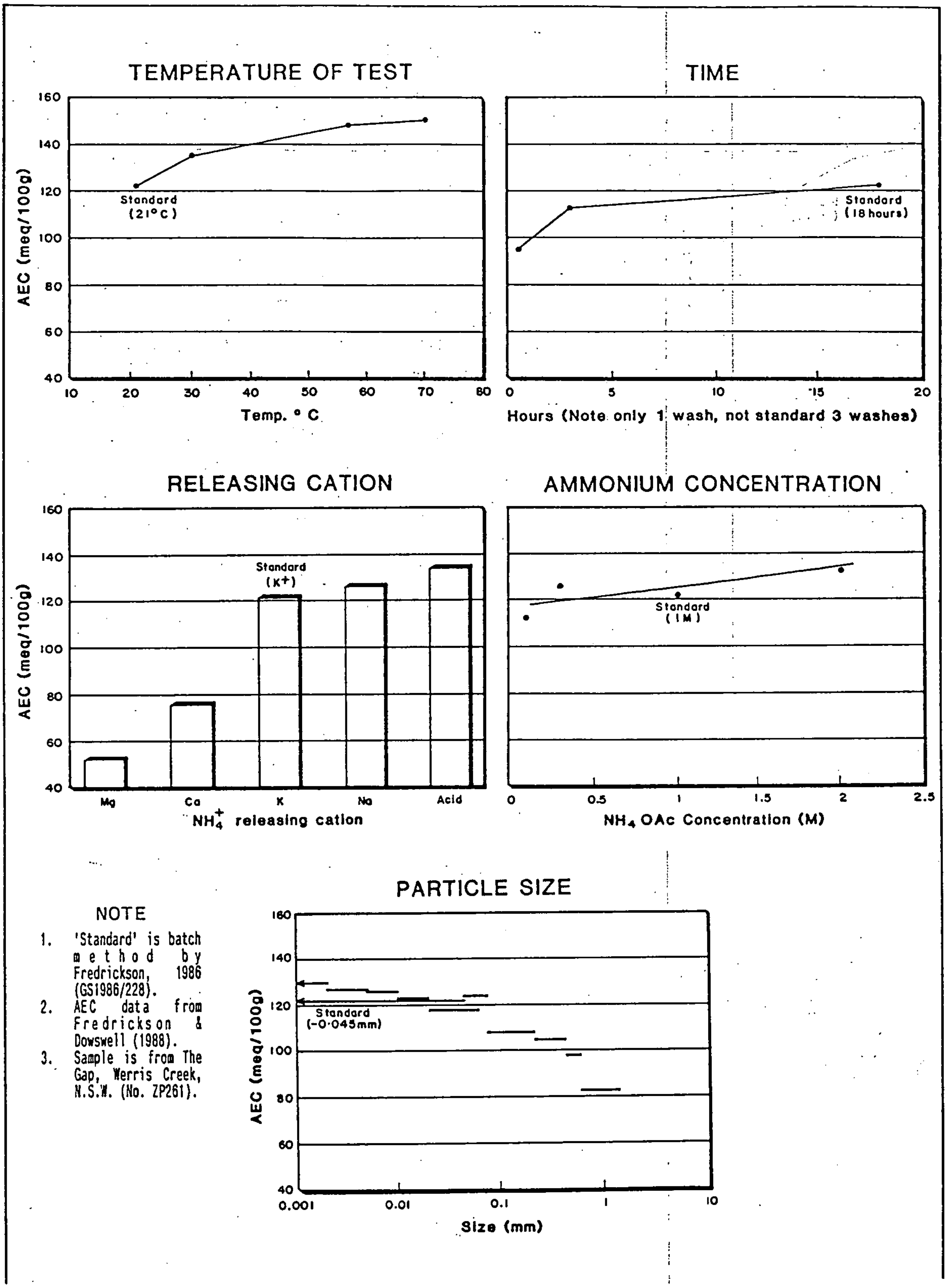


Fig. 21 Some of the factors that influence AEC determination values using Standard technique of Fredrickson, 1986. For comparison, significant AEC is considered over 70 meq/100 g, Australian minimum mine grade 120 meq/100 g.

3.5 BENEFICIATION TRIALS

Commercial beneficiation of zeolitic rocks has been reported for only a couple of overseas authigenic zeolite deposits. The principal published paper on zeolite commercial beneficiation is by Mondale, et al. (1978) dealing with the U.S.A. Bowie zeolite deposit. Enrichment of Neapolitan Yellow Tuff (Italy) in an attempt to obtain possible commercial industrial application material is also reported (De'Gennaro et al., 1983). An attempt at beneficiation of hydrothermal zeolites from basalt breccia voids in Tasmania was unsuccessful (Askins, 1980). For characterisation studies on zeolite crystals, small scale laboratory beneficiation is often mentioned in mineralogical papers (methodology detailed by Ming & Dixon, 1987).

	Light	Mids	Heavy
AEC -45 µm	74,72	68	57
AEC -1 mm	58,60	49	41
CEC -45 µm	99	87	86
SiO_2%	67.5	69.2	70.1
Al_2O_3%	12.7	12.4	12.4
Na_2O%	1.0	1.0	1.3
Exch. Na^+	16	16	16
K_2O%	3.89	4.11	4.32
Exch. K^+	3	3	3
CaO%	2.22	2.02	2.04
Exch. Ca^{++}	69	59	60
MgO%	0.75	0.65	0.50
Exch. Mg^{++}	11	9	7
Fe_2O_2 %	1.50	1.21	1.12
TiO_2+MnO+ SO_3+P_2O_5%	0.30	0.27	0.30
LOI%	9.2	7.9	7.0
Conduct.	190	160	150

Table 2 AEC, CEC and exchanged cations (meq/100g), assay values (%), and conductivity (µS/cm) of tabled fractions.

In an attempt to obtain higher grade economic zeolitic material, a small beneficiation experiment was conducted (Flood, 1988a). From The Gap drillhole WSG-2, 0-18 m low grade core was split and combined, crushed in a rolls crusher and then stage ground in a laboratory rod mill to 75 percent passing 75 µm. The reason for this sizing is that it was also used for the regular powder sold by Zeolite Australia, and thus was economically viable (finer size fractions involve considerably more milling). The ground sample was fed to a laboratory quarter size Wilfley Table and the lights, mids and heavy fractions collected (Amdel, 1987).

After settling and decanting, the three fractions obtained were dried and weighed. Because zeolite has a density (2.2) lower than the gangue minerals (~2.6), the three samples are considered in reverse order from that considered in metalliferous mining, the heavy fraction is considered tailings and the light fraction is concentrate. The following fractions were obtained: Heavy tailing 3.44 kg (30.5%), Middling 2.79 kg (23.9%), Light concentrate 5.43 kg (46.6%), total 11.66 kg.

The NSW Department of Mineral Resource obtained the Standard AEC and the CEC measurements (Fredrickson, et al., 1988, the Lights second AEC values were duplicate samples, L87/1042, L87/1043, Fredrickson, 1987). The higher CEC compared with AEC is correlated with the higher Conductivity, indicating dissolved salts were present.

The whole rock analysis shows the concentrate (lights) is depleted in SiO_2 (by 2.6%), and K_2O (by 0.43%) and enriched in MgO (by 0.25%), CaO (by 0.18%), and higher LOI (by 2.2%), compared to the tailings (heavy). This is to be expected with a small increase in zeolite content.

The AEC shows 22 percent difference between the tailings and the concentrate (-45 μm material). While this appears successful, for commercial separation and concentration, a sizing approximately of over 0.25 mm material would have to be used based on Taggart's expression (Millard, 1993). Thus work to date has shown that gravity separation is possible, but more work on practical sizings (for concentration equipment) needs to be completed.

4. MARKET AND PRODUCT DEVELOPMENT

Market development starts with the products to be provided. Zeolites can be used as absorbents, ion-exchangers, and catalysts, and the full potential utilisation has yet to be fully appreciated. Natural authigenic zeolite products have mineral impurities, differing zeolite contents, diverse zeolites species, variable mineral Si/Al ratios, and inconsistent cation contents, compared to their very expensive synthetic counterparts.

But mineral impurities can act as binders ensuring mechanical strength (Kallo et al., 1982), zeolite species together with Si/Al ratio generally do not significantly change within a given area, and cation composition can easily be modified by simple ion-exchange. This results in the need to treat each potential mine site as a separate product, based on detailed characterisation. From this, different sizings, packaging, ion-exchanges, and other pre treatments generate a whole range of marketable products.

4.1 ZEOLITE APPLICATIONS AND MARKETS

World wide natural zeolite production is estimated at 300,000 tonnes/year (Roskill Information Services Ltd, 1990), with 80-90 percent going into building/construction industry (used as local building stones), agriculture and paper manufacture (used as a filler). The remainder is consumed in the higher value industrial applications, including ceramics, oxygen generation

AGRICULTURE

✓ **Animal Husbandry:** Improves feed conversion in many intensively reared animals; reduces toxic effects of cheap sources of nitrogen in feed (e.g. urea). Reduces incidence of intestinal problems in pigs; improves well-being and egg output in chickens. Reduces malodour in animal sheds; results in drier, more valuable manure.

Agriculture Chemicals: Anti-caking and desiccant use. Helps preserve bagged feed. Acts as slow release carrier for pesticide and chemicals.

✓ **Horticulture:** Improves cation exchange capacity of sandy soils. Acts as slow release medium for cationic nutrients. Reduces need for nitrogenous fertilisers by reducing rate of bacterial nitrification. Active, stable bed for nutrient and moisture control in hydroponics and in potting mixtures. Use as heavy metal trap in association with sewage sludge addition to soils. Addition to composting organic matter helps retain valuable ammonia.

AQUACULTURE

✓ Removes ammonium ions from water in recycle scrubbers, or if added to water or fish food. Use as aquarium gravel. Low cost oxygen generator for pond reoxygenatation and aeration.

BUILDING INDUSTRY

ϴ Dimension stone* or pozolan. Pathway aggregate*. Light weight, acid resistant bricks.

CHEMICAL INDUSTRY

Gas separation and purification. Extensive use (mainly synthetic zeolites) in petroleum and petrochemical industry for catalytic processes including Hydrogenation and Dehydrogenations, Hydrodealkylation, Methanation, Shape-selective reforming, Dehydration of gases and organic liquids, Organic catalysis; the following inorganic reactions, H_2S Oxidation, NH_3 Reduction of NO, CO oxidation, H_2O dissociation; also hydrocarbon conversion by Alkylation, Cracking, Hydrocracking and Isomerization.

DETERGENT INDUSTRY

Added to powder detergents to displace phosphates for water softening.

DOMESTIC USES

✓ Used as domestic pet litter to absorb moisture and odours. Odour absorbents for refrigerators, shoes, etc. Beverage carbonation. Incorporated around car widows to suppress misting.

ENERGY TECHNOLOGY

Alternative Fuels: Expanding use of new synthetic, high-silica zeolites for catalytic conversion of simple organic chemicals (e.g. methanol) to high octane fuels.

Gas supply: Clean gases from garbage dumps etc to supply methane fuel.

Solar Power: Convert solar energy into thermal energy by hydration-dehydration, use as heat storage medium for solar heating or cooling.

FOOD INDUSTRY

✓ Filter aid for purifying and clarifying (e.g. wine or sugar solutions). In plastic wraps improves shelf life of fruit and vegetables.

MANUFACTURING INDUSTRY

Filler in paper* and reactive absorbent/filler in many plastic and rubber goods. Storage of H_2, CH_4, argon and krypton for welding rods, etc. Solid state batteries and conducting paper. Pressure swing process for low capital cost oxygen or nitrogen generation. Feed material for ceramics manufacture.

MEDICAL APPLICATIONS

Polishing agent in fluoride containing toothpaste, in kidney dialysis systems to separate ammoniacal nitrogen from haemodialysis liquids.

POLLUTION CONTROL

ϴ **Water Treatment:** Ammonium removal from agricultural liquid effluents and from treated sewage water. Radioactive Cs and Sr removal from nuclear waste waters. Heavy metal removal from mining and metallurgical wastes and garbage dump effluents. Absorbent for oil and grease spills. Useful in softening of water.

Gas "Clean Up": Removal of water and simple polar pollutant gases from stack gases and gases evolved from garbage dumps. As moisture absorbent in some car exhaust systems.

ϴ **Flame Extinguishers:** Can release H_2O, CO_2 or organic halides, high cooling effect, forms smothering glass on pyrophoric metals.

WEATHER MODIFICATION

Crystallisation nuclei for water and water vapour, possibly for seeding clouds.

* Use may not necessarily depend on the presence of zeolite in the host rock, but rather on the physical nature (availability, density, colour, porosity) of the host rock.

Table 3. Applications of zeolites. ✓ indicates commercial sale in Australia established, ϴ indicates trials started and waiting for acceptance.

plants, solar heating/cooling, catalysts, sewerage water cleaning, radioactive waste control etc.

Table 3 presents the numerous and diverse current and proposed markets for zeolites, both synthetic and natural. Also shown are those where Australian natural zeolites are currently undergoing trial, together with those where commercial sales are already established. The papers by Mumpton (1978) and by Breck (1980) provide a comprehensive review of possible applications.

There is no controlled or organised market for zeolites; buyers negotiate directly with known producers. Most producers try to constantly promote the use and consumption of zeolites, but this is uncoordinated. Mining of zeolites now occurs in over 17 countries, including Japan, Cuba, China, Mexico, United States, Italy, and former USSR States. A complicating factor is that no standard testing or product description exists, sometimes resulting in less than acceptable results for clients, due to the various chemical and physical natures of natural zeolites.

4.2 HEALTH STUDIES

One of the more serious potential threats to the further development of natural zeolite markets is the association of (certain fibrous) zeolites and the development of mesothelioma. Epidemiological data shows that exposure to the fibrous zeolite mineral erionite within dusts, even in low exposures, increases the risk of mesothelioma. Guthrie (1992) provides a good review of the biological effects of zeolites using terms familiar to mineral scientists. As there is a trace of fibrous mordenite at Escott, a sample of ultrafine powder (<50 μm) material was examined by SEM (Fig. 22), and revealed subangular, blocky fragments, down to 1 μm in diameter. This checking for fibrous minerals should be routine for new deposits.

Figure 22 SEM picture of Escott ultrafine powder (<50 μm), note subangular to subrounded blocky particle shapes. Scale bar = 0.1 mm.

A threat to the development of the world natural zeolite market is the unchecked mining of fibrous zeolites. Given the medical literature that is accumulating, it is only a matter of time before compensation cases appear from fibrous zeolite use. Negative publicity is likely to result, possibly being targeted at zeolites as a whole, regardless of which zeolite minerals are present. Unless zeolite producers actively and continually state the zeolite type and crystal habit being mined, confusion will occur in the community. Zeolite is a group term, and consumers should be both aware of this terminology, and be informed exactly what zeolites they will be receiving. Fibrous zeolites, in particular erionite, should not be mined or the cost could be the reputation of the remaining natural zeolite mining industry.

4.3 PRICING AND COSTS

No product will sell if the price is perceived to exceed the value of the product by the client. Current pricing is based around a benchmark of $160/tonne, FOB, Mudgee N.S.W, for full truck load (20 to 22 tonnes) for regular powder in 20 kg paper sacks. Other products and amounts are more expensive or cheaper depending on analysis of production costs (handling, bag costs, time required etc.).

Of the direct operation costs, freight and crushing/screening/milling are the major costs. For the first six years, 38 percent of total invoiced income was consumed by freight paid by Zeolite Australia, and 33 percent went towards contract milling/crushing/bagging. Actual mining costs are low (around 5%), as is the 2.3 percent of zeolite income that went to the landholder as compensation. Another cost is that a large proportion of tonnes mined do not generate income (only 70 percent of tonnes mined were sold), due to samples, trials, shrinkage, loss etc. Given the cost percentage, little is left from the invoiced income for overheads including marketing, research, advertising etc.

For Escott Natural Zeolite sold in the first six years, the average freight paid for the delivery of raw material to milling plants alone was $36/tonne (some of this is recovered as the mill may be closer to some clients). In order that this component of costs is reduced, the new milling plant site is located near the township of Werris Creek, central to the current and proposed N.S.W. mining locations. Also Zeolite Australia is actively engaged in negotiations with freight companies to minimise freight costs. This includes arranging with the smaller clients that their part loads can go together as split loads, thereby getting the full truck discounted freight rates. To ensure compatibility for all parties, time is required for organisation, but it ensures that markets are encouraged to maximise their use of natural zeolites.

One example of this is the Western Australian distributor, a distance of 3825 kilometres to Perth from Werris Creek by road. When the first truck load was delivered by roadfreight the cost was $262/tonne, the next shipment by slower sea container resulted in a freight cost of only $102/tonne. This has since been further reduced, resulting in a lower cost to the Western Australian distributor, who in turn has responded by more active promotion of the product.

The other main cost is milling. Unlike many overseas deposits where mining can be done by ripping with dozers, the Australian zeolite has to be drilled and blasted, followed by crushing, screening, and, depending on product required, milling. The processing costs have been determined by the availability of suitable contractors. Cost for milling alone for the regular powder (<100 µm) has over the last six years averaged $48/tonne, with individual batches costing up to $94/tonne. The main problem was the availability of milling during peak client demand, resulting in the use of more expensive mills to satisfy the demand. This variability in costs has been absorbed by Zeolite Australia.

4.4 MARKETING APPROACH

Since the mining of zeolite had become the sole mining activity for Mount Gipps Limited, following the termination of other exploration and mining activities, Mount Gipps Limited changed its name in August 1992 to Zeolite Australia Limited. This name change was to reflect the change in focus of the company to pursue an intensive marketing and development phase for natural zeolite.

Early marketing research was conducted by a group of agricultural consultants and saw zeolite marketed largely into stockfeeds, potting mixes and organic fertilisers. Further developments were focussed on industrial applications for sewerage treatment and water filtration.

Since mid-1992, there has been a change in focus with an increase in both research and development of zeolite applications, and of marketing. The change has seen Zeolite Australia Limited market zeolite product through three distinct channels as listed below in Table 4 (see Marx, et al., 1993, for more in depth discussion).

CHANNEL	NOTES
MANUFACTURERS (produces new product incorporating zeolite)	Manufacturing companies in the areas of organic and, chemical fertilisers, potting mixes, stockfeeds and stockblocks, aquarium gravel, kitty litter and odour control products. Initial research data provided by Zeolite Australia Limited led to trialing by these companies prior to their commercialisation of products containing zeolite. Companies undertake their own advertising and promotion with some technical input from Zeolite Australia Limited.
DISTRIBUTORS (on sells zeolite as received)	Initially a small distribution system was set up mainly for marketing retail packs to home and market gardeners. A major success of this system was the contact with manufacturers who sourced initial trial product via this network. Distributors have been set up to handle home garden, horticulture, turf, aquaculture and specialty retail products. In most cases distributors handle products for only one or two markets with very little overlap. Advertising and promotion is undertaken by joint arrangements with Zeolite Australia Limited.
INDUSTRIAL USERS (consumes zeolite in final end use)	Due to high transport costs, large industrial users such as sewage works, swimming pools and other end uses, will be supplied direct or via industrial contracting companies. Zeolite Australia is to be more active in the development and licensing of this environmental application technology, with recent acquisitions of patented process for waste water treatment and water filtration using zeolite filters and zeolite bio-filters.

Table 4. Marketing channels used by Zeolite Australia Limited for Escott Natural Zeolite.

RESEARCH AND DEVELOPMENT

The development of technological innovations leading to processes that utilise natural zeolites to deliver economic and environmental benefits is important to the future of Zeolite Australia. Nearly all research is into the application of zeolites.

Many research projects are currently underway in the following areas; new fertiliser products for slow release of nutrients specifically aimed at sugar cane, tropical fruit, cut flowers and vegetables; zeolite as a soil amendment for turf construction and renovation; zeolite use to improve fertiliser value of composted animal manures and effect on soil nutrition; zeolite use to improve N+K retention and reduce leaching in potting mixes; ammonia removal in saltwater and freshwater aquaculture; heavy metal stabilisation in soils and wastes; sewage sludge stabilisation; ammonia removal in ion exchange column; and use of zeolite in biological wetlands filters. Many more industrial applications are only now being appreciated.

Research is continuing with databases being built containing bibliographic references of zeolite applications (ZEOREF), and chemistry and mineralogy of Australian and overseas zeolites (ZEOCHEM). All samples, trials, and sale details are databased (ZEOSYS) so that analysis can be done on research, marketing, and sales performance.

Basic research needed includes the generation of cation exchange isotherms (see Semmens, 1984) for common expected solutions, thus enabling the prediction of effective zeolite capacity, and consequently the required zeolite dosages necessary for specific applications. Examples of required selectivity coefficients, which is similar to an equilibrium constants and from which the exchange isotherms are built, are NH_4^+-Na^+, NH_4^+-K^+, NH_4^+-Ca^{2+}, Na^+-K^+, Na^+-Ca^{2+}, K^+-Ca^{2+}.

Recent trial feedback indicates that Escott Natural Zeolite appears to prevent boron deficiency in carnations during commercial cut flower growing conditions. The influence of zeolites with trace metals in agriculture is unknown. No published papers deal with this subject, yet it is an area of potential market interest. In this case it is likely that the zeolite is reacting with the boron chemical already added, and releasing the boron so as to be available to the plants. But this is an example of an area where research is needed.

4.5 ECONOMICS OF THE AUSTRALIAN ZEOLITE MARKET

The Australian zeolite mining industry has been operating at a loss since mining began in December 1987. Most of the costing problems are directly associated with problems of scale of operation. Without higher tonnages, turnover costs per tonne are difficult to reduce.

Until the market grows and stabilises, and sufficient capital is injected, operating costs will be detrimentally high. Currently the market has matured to the stage where sales are now independent of any single end user category (Marx et al., 1993), but each market segmentation requires individual product specifications, packaging, distribution network, technical and trial support.

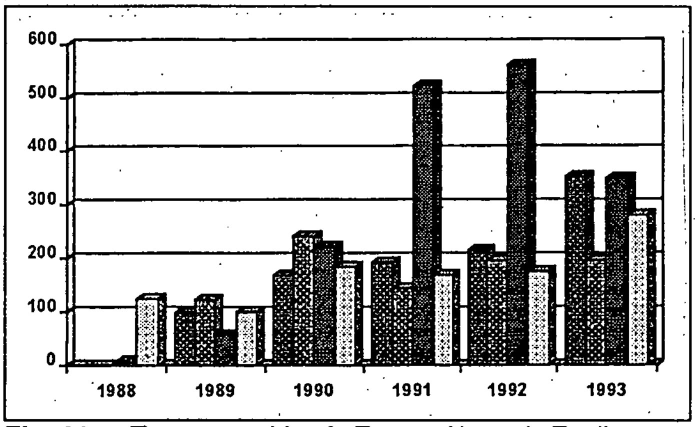


Fig. 23 Tonnes sold of Escott Natural Zeolite per quarter for the first six years based on order date.

The 3 December 1993 marks the sixth anniversary of zeolite mining in Australia, with a total of 6672.3 tonnes of ore mined since operations begun. It took six months to generate the first sale (for aquaculture), but since then a total of 4657.5 tonnes have been sold up till 3 December 1993, with sales steadily growing as is shown in Figure 23.

Sales have been predominantly to the animal feed and horticulture markets (Fig. 24) during the last six years, but other areas are growing. One aspect that is very different from metalliferous mines is the number and diversity of clients. In the first six years commercial sales have been made to over 230 different customers, scattered across Australia, and overseas (Fig. 24). In 1991 some large organic fertiliser manufactures began incorporating zeolite into their products, and this can be seen in the June-August quarter orders as this market is seasonal (during 1993 these larger clients averaged out their orders over the year). In other markets the orders reflect advertising expenditure (domestic gardens), and in others (i.e. piggeries) orders are dependant on the client products market performance (i.e. pork markets), indicating that zeolite is considered a luxury item, which can be done without when times are bad.

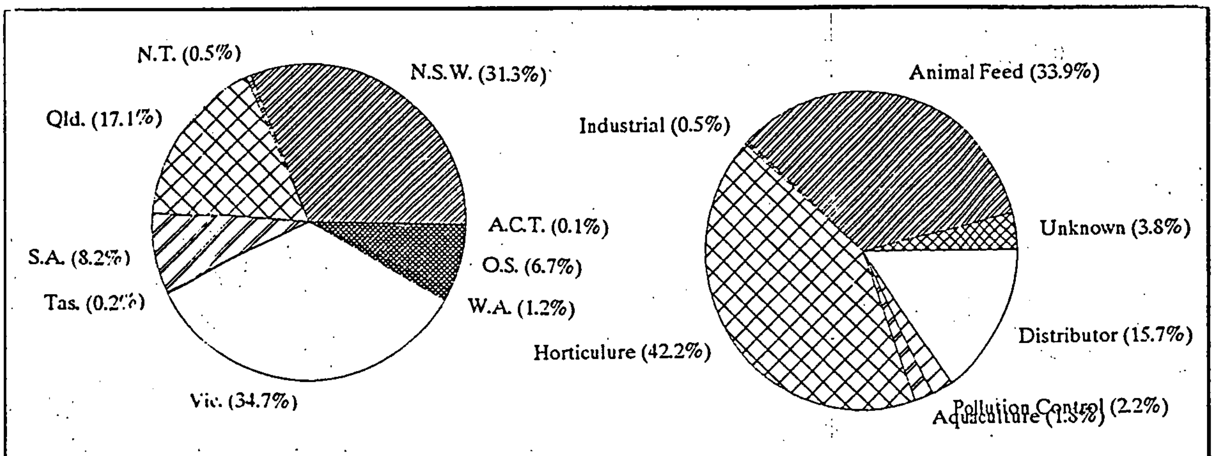


Fig. 24 Percentage tonnes sold by market category, and delivery address, for the first six years of production.

The problem to date has been the lack of consumer and investor knowledge, and confidence, in natural zeolites. This is combined with low tonnages resulting in extremely low efficiency (high shrinkage and loss, higher operating cost/tonne).

There is no question that sales are price sensitive, and that different market categories show differences in their sensitivity too price changes. In some areas the prices needs to be lowered to encourage trial and acceptance. The approach that has been adopted is to proceed with acquiring a dedicated zeolite processing plant at Werris Creek, which will resolve many cost problems. The other approach under way is to further develop other markets, particularly high priced value added products.

In summary, the development of natural zeolite markets have encountered difficulties in the area of production costs and marketing. Zeolite Australia Limited continues to progress the sales of natural zeolite despite the following problems (after Marx et al., 1993):

1. Reluctance by industries to adopt innovations;
2. Cost to the company of demonstrating innovations to third parties;
3. Little assistance in development costs from either public or private funding;

4. Expensive initial contracted milling operations;
5. Vast distances resulting in high freight component of final end user price;
6. Threat of new local producers of zeolite entering market after expensive acceptance phase has been borne by initial developer;
7. Cost of training a distribution network; and
8. Severe recession in both agricultural and industrial sectors in Australia over past 5 years.

5. CONCLUSIONS

The development of a natural zeolite industry is no longer dependent on geological investigations, but has developed to where the industry is now dependent on marketing and application research. Thus Zeolite Australia Limited has become involved in the development, acquisition, and licensing of technology for environmental applications of natural zeolite. The most important change taking place in developed countries like Australia is the growing awareness and concern of the general public towards the environment. Natural zeolites through numerous applications can become one of the leading products in the promotion of more sustainable less environmentally damaging agricultural and industrial developments.

Both exploration, and corresponding geological research have been a very low priority in the development of a stable natural zeolite market in Australia. As has been the Cuban experience with zeolite market development (Gonzalez & Costa De Los Reyes, 1993), no matter how large or pure the ore deposit, it is detailed information on the product's application behaviour that is required by the markets. No two zeolite deposits are the same, and detailed characterisation of further deposits is essential. To help develop more standards for characterising natural zeolites, an International Zeolite Marketing Board where member companies can trade technological developments with other members should be encouraged. This board could develop a set of standards for classifying the characteristics, both chemically and physically, of zeolites and zeolitic products, to simplify local interpretation of overseas research papers. All suppliers of zeolites should be able to provide mineralogical and physical details about their products.

A more serious potential threat to the greater development of natural zeolite markets is the association of fibrous erionite zeolite with mesothelioma. This mineral is considered in recent publications to have higher toxicity than asbestos (Guthrie, 1992). Fibrous zeolites, in particular erionite, should not be mined or the cost could be the reputation of the remaining natural zeolite industry.

Given time there remains much to learn about Australian zeolites, their chemistry and properties. This work is just the starting point. The natural zeolite industry in Australia is established, but growth will be slow and difficult due to high costs and depressed consumer appreciation. The role of the geologist has moved from active exploration, to that of technical coordinator for a mineral group with extremely wide applications.

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SAMPLE NUMBER	SAMPLE TYPE	LOCATION	SAMP. BY	BATCH	AEC meq	SiO2 %	TiO2 %	Al2O3 %	Fe2O3 %	FeO %	MnO %	MgO %	CaO %	Na2O %	K2O %	P2O5 %	SO3 %	LOI %	TOTAL %	LAB
WSE 1 29-44m	Drill Chips	Escott	PF	MRDL 87/53	91	68.20	0.13	11.50	1.00	0.20	0.01	1.05	2.90	1.00	1.63	0.02	0.10	11.40	99.00	MRDL
Z3 (1/1988)	Milled Sample	Escott	SC	Z3 Bulk	130	68.26	0.23	12.99	1.37		0.06	0.83	2.09	0.64	4.11	0.06	0.00	8.87	99.51	U.N.E.
WSE 2 29-41m	Drill Chips	Escott	PF	MRDL 87/53	109	67.90	0.12	11.70	1.20	0.20	0.01	1.10	3.01	1.00	1.39	0.04	0.10	12.20	99.90	MRDL
WSE 2 35-41m	Drill Chips	Escott	PF	MRDL 87/53	115	67.20	0.12	11.80	1.20	0.20	0.01	1.15	3.04	1.10	1.19	0.03	0.10	12.70	99.70	MRDL
ZP310	Rock Chip	Escott	SP	MRDL 87/53	105	72.40	0.09	10.20	0.60	0.10	0.01	1.00	2.99	0.60	0.78	0.05	0.10	11.50	100.30	MRDL
ZP308	Rock Chip	Escott	SP	MRDL 87/53	124	67.40	0.17	12.00	0.70	0.20	0.01	1.05	3.46	0.90	1.07	0.09	0.10	12.80	99.80	MRDL
ZP311	Rock Chip	Escott	SP	MRDL 87/53	108	71.10	0.13	10.40	0.70	0.10	0.01	0.90	2.97	0.70	1.23	0.05	0.10	11.00	99.30	MRDL
ZP309	Rock Chip	Escott	SP	MRDL 87/53	115	67.20	0.13	12.10	1.00	0.10	0.01	1.20	3.15	1.00	1.09	0.05	0.10	12.80	99.80	MRDL
Cu 4A 2.0-3.0m	Drill Chips	Sheedy Unit B	RH	25/5/93	159	67.70	0.37	13.31	1.81		0.03	1.45	3.06	1.51	1.00	0.05	0.01	9.10	99.68	Melb Uni
Cu 4A 3.0-5.0m	Drill Chips	Sheedy Unit B	RH	25/2/91 #1	139	63.09	0.40	13.15	2.04	0.00	0.06	1.85	3.30	1.32	1.01	0.06	0.00	13.55	99.82	U.N.E.
Cu 4A 3.0-5.0m	Drill Chips	Sheedy Unit B	RH	25/2/91 #2	139	62.98	0.39	13.16	2.04	0.00	0.06	1.84	3.30	1.35	1.03	0.06	0.00	13.58	99.79	U.N.E.
SH 1A 0.0-7.4m	Channel	Sheedy Unit B	RH	25/2/91 #2	132	65.06	0.39	12.69	1.63	0.00	0.03	1.49	3.69	0.59	1.08	0.06	0.01	12.89	99.60	U.N.E.
SH 1A 0.0-7.4m	Channel	Sheedy Unit B	RH	25/2/91 #1	132	64.89	0.39	12.70	1.63	0.00	0.03	1.50	3.67	0.57	1.08	0.06	0.00	12.88	99.39	U.N.E.
Cu 6A 2.0-4.0m	Drill Chips	Sheedy Unit C	RH	25/5/93	142	68.89	0.31	12.79	1.52		0.04	1.17	3.49	1.11	1.42	0.05	0.01	8.68	99.69	Melb Uni
ZP261	Rock Chip	The Gap	SP	MRDL 87/35	122	66.30		13.10	1.14			0.50	2.61	2.50	2.46			9.20	98.11	MRDL
ZP315	Rock Chip	The Gap	SP	MRDL 87/53	75	68.00	0.21	12.90	0.80	0.10	0.01	0.65	2.05	0.80	4.99	0.05	0.10	8.20	98.80	MRDL
ZP317	Rock Chip	The Gap	SP	MRDL 87/53	76	69.50	0.17	12.00	0.90	0.10	0.01	0.40	2.05	0.70	5.12	0.06	0.10	7.40	98.40	MRDL
ZP318	Rock Chip	The Gap	SP	MRDL 87/53	79	69.90	0.17	11.60	0.70	0.20	0.01	0.70	2.65	1.20	2.38	0.06	0.10	9.50	99.10	MRDL
ZP325	Rock Chip	The Gap	SP	MRDL 87/53	116	67.70	0.18	12.30	1.50	0.10	0.02	0.35	2.13	0.80	4.74	0.05	0.10	8.50	98.40	MRDL
ZP332	Rock Chip	The Gap	SP	MRDL 87/53	119	67.00	0.19	13.00	1.20	0.10	0.04	0.45	2.61	2.20	2.76	0.01	0.10	10.20	99.70	MRDL
ZP334	Rock Chip	The Gap	SP	MRDL 87/53	72	70.10	0.13	12.30	1.00	0.10	0.03	0.65	2.53	1.10	3.44	0.02	0.10	8.30	99.60	MRDL
ZP312	Rock Chip	The Gap	SP	MRDL 87/53	71	70.50	0.18	12.00	0.90	0.10	0.01	0.55	1.84	1.00	4.57	0.05	0.10	7.20	98.90	MRDL
ZP326	Rock Chip	The Gap Unit B	SP	MRDL 87/53	129	66.80	0.19	12.50	0.90	0.10	0.03	0.45	2.66	2.20	2.23	0.05	0.10	9.90	98.00	MRDL
ZP327	Rock Chip	The Gap Unit B	SP	MRDL 87/53	83	70.80	0.16	11.80	1.20	0.10	0.05	0.75	1.63	2.50	2.12	0.07	0.10	7.90	99.00	MRDL
ZP329	Rock Chip	The Gap Unit B	SP	MRDL 87/53	91	70.50	0.16	11.50	1.10	0.10	0.04	0.60	2.28	1.90	1.95	0.06	0.10	8.20	98.30	MRDL
ZP307	Rock Chip	Lower Quipolly	SP	MRDL 87/53	98	77.40	0.16	8.40	0.60	0.10	0.02	0.30	1.67	2.20	0.43	0.06	0.10	7.00	98.30	MRDL
ZP306	Rock Chip	Lower Quipolly	SP	MRDL 87/53	117	65.80	0.26	12.90	1.30	0.10	0.01	1.05	2.67	1.70	0.83	0.07	0.10	12.40	99.10	MRDL
ZP253	Rock Chip	Melville Range	SP	MRDL 87/35	116	66.10		12.50	1.68			0.70	4.67	0.70	1.19			11.10	99.04	MRDL
ZP302	Rock Chip	Quipolly Dam	SP	MRDL 87/53	104	67.70	0.20	12.70	1.10	0.10	0.01	1.20	3.12	1.60	1.06	0.07	0.10	11.10	99.90	MRDL
ZP304	Rock Chip	Quipolly Dam	SP	MRDL 87/53	76	66.60	0.28	14.40	1.70	0.20	0.01	1.25	3.34	2.40	1.04	0.10	0.10	9.80	101.10	MRDL
LOCATION SUB TOTALS		ESCOTT		Mean		68.71	0.14	11.59	0.97	0.16	0.02	1.03	2.95	0.87	1.56	0.05	0.09	11.66	99.66	
(If n>1)				Stand Deviation		1.95	0.04	0.91	0.28	0.05	0.02	0.12	0.39	0.19	1.06	0.02	0.04	1.32	0.40	
				Sample Count		8	8	8	8	7	8	8	8	8	8	8	8	8	8	
		SHEEDY, UNIT B		Mean		64.74	0.39	13.00	1.83	0.00	0.04	1.63	3.40	1.07	1.04	0.06	0.00	12.40	99.66	
				Stand Deviation		1.92	0.01	0.29	0.21	0.00	0.02	0.20	0.27	0.45	0.04	0.00	0.00	1.88	0.17	
				Sample Count		5	5	5	5	4	5	5	5	5	5	5	5	5	5	
		GAP, MAIN UNIT		Mean		68.63	0.18	12.40	1.02	0.11	0.02	0.53	2.31	1.29	3.81	0.04	0.10	8.56	98.88	
				Stand Deviation		1.58	0.02	0.55	0.26	0.04	0.01	0.13	0.32	0.68	1.17	0.02	0.00	1.03	0.57	
				Sample Count		8	7	8	8	7	7	8	8	8	8	7	7	8	8	
		GAP, UNIT B		Mean		69.37	0.17	11.93	1.07	0.10	0.04	0.60	2.19	2.20	2.10	0.06	0.10	8.67	98.43	
				Stand Deviation		2.23	0.02	0.51	0.15	0.00	0.01	0.15	0.52	0.30	0.14	0.01	0.00	1.08	0.51	
				Sample Count		3	3	3	3	3	3	3	3	3	3	3	3	3	3	
		OTHER SITES		Mean		68.72	0.22	12.18	1.28	0.13	0.01	0.90	3.09	1.72	0.91	0.08	0.10	10.28	99.49	
				Stand Deviation		4.91	0.06	2.24	0.46	0.05	0.00	0.40	1.09	0.66	0.30	0.02	0.00	2.05	1.06	
				Sample Count		5	4	5	5	4	4	5	5	5	5	4	4	5	5	
CURRABUBULA FORMATION		ALL SAMPLES		Mean		68.10	0.21	12.21	1.21	0.11	0.02	0.94	2.82	1.30	2.01	0.05	0.08	10.33	99.30	
AEC > 70 meq/100g				Stand Deviation		2.84	0.10	1.11	0.41	0.06	0.02	0.42	0.68	0.63	1.40	0.02	0.04	2.07	0.70	
All Whole Rock				Sample Count		30	28	30	30	25	28	30	30	30	30	28	28	30	30	

ZP samples from NSW Department of Mineral Resources, Fredrickson & Pecover, 1987

APPENDIX 1 Whole rock major element analysis for selected zeolitised samples from Currabubula Formation, Tamworth Belt, N.S.W.

SAMPLE NUMBER	SAMPLE TYPE	LOCATION	SAMP. BY	BATCH	ABC meq	Ag ppm	As ppm	Au ppm	Ba ppm	Be ppm	Bi ppm	Ce ppm	Cl ppm	Co ppm	Cr ppm	Cs ppm	Cu ppm	P ppm	Ga ppm	Hf ppm	Hg ppm	La ppm	Li ppm	Mn ppm	Mo ppm	Nb ppm	Nd ppm	Ni ppm	Pb ppm	Rb ppm	Sb ppm	Sc ppm	Sn ppm	Sr ppm	Th ppm	U ppm	V ppm	Y ppm	Zn ppm	Zr ppm	LAB
Z3 (1/198)	Milled Sample	Escott	SC	R1967	130		10										5									12			10	63			11	739				52	73	259	Unisearch
Z3 (1/1988)	Milled Sample	Escott	SC	Z3 Bulk	130				1385			86			11	5	2		16			39		528		10	39	2	22	119		2		1339	14	4	15	38	63	225	U.N.E.
WSB 2 29-41m	Drill Chips	Escott	PF	MRDL 87/53	109				474		2	75			3	6	13		15	3		33		244	5	16	41	2	24	58	4	4	4	654	19	2	13	55	63	193	MRDL
WSB 2 35-41m	Drill Chips	Escott	PF	MRDL 87/53	115	2		0.03	665	2	2	72	100		5	7	13	170	16	3	0.03	30	15	242	5	17	38	1	26	52	4	6	4	661	20	2	13	48	64	189	MRDL
Z3UB (1/1988)	Milled Sample	Escott	SC	R1967	106		11										2									12			7	77	1			868				53	67	239	Unisearch
WSB 1 29-44m	Drill Chips	Escott	PF	MRDL 87/53	91				2223		2	76			2	5	18		15	3		33		214	5	17	33	1	23	71	5	4	4	463	19	4	12	58	66	201	MRDL
ZP308	Rock Chip	Escott	SP	MRDL 87/53	124	2		0.03	964	2	2	69	100		1	5	2	140	11	3	0.02	42	15	130	5	7	32	4	23	52	4	4	4	605	12	1	12	19	28	176	MRDL
ZP309	Rock Chip	Escott	SP	MRDL 87/53	115				596		2	73			1	5	2		15	3		33		159	5	19	37	3	15	41	4	5	4	1039	19	3	10	34	43	209	MRDL
ZP310	Rock Chip	Escott	SP	MRDL 87/53	105				505		2	74			1	6	2		12	3		35		98	5	15	35	3	24	30	5	4	4	852	18	3	8	45	27	163	MRDL
ZP311	Rock Chip	Escott	SP	MRDL 87/53	108	2		0.03	259	7	2	91	100		1	5	2	60	13	3	0.01	43	15	158	5	15	44	2	25	36	4	4	4	483	16	5	5	60	43	213	MRDL
Cu 4A 2.0-3.0m	Drill Chips	Sheedy Unit B	RH	21/5/93	159		5		1080			55	16	<2	18		10		18						0	8	25	35	21	34		5		1177	11	0	19	26	54	254	Melb Uni
Cu 6A 2.0-4.0m	Drill Chips	Sheedy Unit C	RH	21/5/93	142		8		854			60	13	<2	8		8		17						3	10	32	37	26	45		5		614	16	4	13	33	57	262	Melb Uni
ZP318	Rock Chip	The Gap	SP	MRDL 87/53	79	2		0.03	1036	2	2	85	100		1	5	2	290	13	3	0.01	43	20	146	5	8	43	4	17	88	4	5	4	972	13	1	7	33	48	205	MRDL
ZP261	Rock Chip	The Gap	SP	MRDL 87/35	122				740							15	2							320				3	20	85				580					50		MRDL
ZP312	Rock Chip	The Gap	SP	MRDL 87/53	71	2		0.03	1066	4	2	89	100		1	7	5	130	14	3	0.01	47	20	200	5	9	47	3	18	114	4	7	4	1067	12	1	7	33	57	211	MRDL
ZP317	Rock Chip	The Gap	SP	MRDL 87/53	76				984		2	89			1	5	2		14	4		46		252	5	9	44	4	17	115	4	6	4	845	13	1	8	34	48	209	MRDL
ZP325	Rock Chip	The Gap	SP	MRDL 87/54	116	2		0.03	1136	2	2	98	100		1	16	5	190	12	3	0.01	57	15	376	5	9	58	4	15	111	4	6	4	1924	14	1	4	40	42	210	MRDL
Z1 (1/1988)	Milled Sample	The Gap	SC	R1967	108		31										8									10			11	113			4	649				43	75	272	Unisearch
Z1UB (1/1988)	Milled Sample	The Gap	SC	R1967	101		26																			8			11	110				788				40	68	262	Unisearch
Z2UB (1/1988)	Milled Sample	The Gap	SC	R1967	77		15										1									9				128				1109				45	67	314	Unisearch
ZP315	Rock Chip	The Gap	SP	MRDL 87/53	75	2		0.03	1410	3	2	92	100		1	5	4	140	14	3	0.01	48	15	127	5	10	48	4	20	123	4	5	4	1423	14	1	10	37	45	223	MRDL
ZP326	Rock Chip	The Gap Unit B	SP	MRDL 87/54	129				767		2	105			1	13	2		12	3		48		540	5	10	52	3	18	87	4	8	4	557	15	1	7	37	55	227	MRDL
ZP327	Rock Chip	The Gap Unit B	SP	MRDL 87/54	83				1424		2	69			1	9	3		11	3		33		620	5	6	26	4	10	55	4	4	4	2131	10	1	7	26	34	146	MRDL
ZP329	Rock Chip	The Gap Unit B	SP	MEDL 87/54	91				1006		2	67			1	12	3		10	3		30		574	5	6	28	4	17	45	4	4	4	1607	13	1	7	26	28	142	MRDL
ZP253	Rock Chip	Melville Range	SP	MRDL 87/35	116				950							10	2							390				5	15	65				1110					60		MRDL
LOCATION SUB TOTALS		ESCOTT		Mean		2.0	10.5	0.03	883.9	3.7	2.0	77.0	100.0		3.1	5.5	6.1	123.3	14.1	3.0	0.02	36.0	15.0	221.6	5.0	14.0	37.4	2.3	19.9	59.9	3.9	4.1	4.9	770.3	17.1	3.0	11.0	46.2	53.7	212.2	
(If n>1)				Stand Deviation		0.0	0.7	0.00	641.8	2.9	0.0	7.5	0.0		3.5	0.8	6.1	56.9	1.9	0.0	0.01	4.8	0.0	134.4	0.0	3.7	4.0	1.0	6.7	25.5	1.2	1.1	2.5	267.2	2.9	1.3	3.2	12.7	15.9	37.9	
				Sample Count		3	2	3	8	3	7	8	3	0	8	8	10	3	8	7	3	8	3	8	7	10	8	8	10	10	8	8	8	10	8	8	8	10	10	10	
		GAP, MAIN		Mean		2.0	24.0	0.03	1062.0	2.8	2.0	90.6	100.0		1.0	8.8	3.6	187.5	13.4	3.2	0.01	48.2	17.5	236.8	5.0	9.0	48.0	3.7	16.1	109.7	4.0	5.8	4.0	1040.2	13.2	1.0	7.2	38.1	55.6	238.3	
				Stand Deviation		0.0	8.2	0.00	217.7	1.0	0.0	4.8	0.0		0.0	5.2	2.3	73.2	0.9	0.4	0.00	5.3	2.9	98.2	0.0	0.8	6.0	0.5	3.6	14.4	0.0	0.8	0.0	419.5	0.8	0.0	2.2	4.6	11.8	40.0	
				Sample Count		4	3	4	6	4	5	5	4	0	5	6	8	4	5	5	4	5	4	6	5	8	5	6	8	9	5	5	6	9	5	5	5	8	9	8	
		GAP, UNIT B		Mean					1065.7		2.0	80.3			1.0	11.3	2.7		11.0	3.0		37.0		578.0	5.0	7.3	35.3	3.7	15.0	62.3	4.0	5.3	4.0	1431.7	12.7	1.0	7.0	29.7	39.0	171.7	
				Stand Deviation					332.5		0.0	21.4			0.0	2.1	0.6		1.0	0.0		9.6		40.1	0.0	2.3	14.5	0.6	4.4	21.9	0.0	2.3	0.0	801.5	2.5	0.0	0.0	6.4	14.2	48.0	
				Sample Count		0	0	0	3	0	3	3	0	0	3	3	3	0	3	3	0	3	0	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	
CURRABUBLA FORMATION		ALL SAMPLES		Mean		2.0	15.1	0.03	976.2	3.1	2.0	79.2	81.0	0.0	3.3	7.8	4.9	160.0	13.8	3.1	0.01	40.0	16.4	295.4	4.6	11.0	39.0	6.4	18.1	76.7	3.9	4.9	4.4	970.4	14.9	2.0	9.8	39.8	53.0	220.0	
ABC > 70 meq/100g				Stand Deviation		0.0	9.7	0.00	429.5	1.9	0.0	13.4	37.7	0.0	4.6	3.8	4.5	70.2	2.2	0.3	0.01	7.9	2.4	169.9	1.3	3.7	9.0	10.2	5.6	32.1	0.9	1.4	1.7	438.1	3.0	1.5	3.9	11.0	14.2	43.6	
Whole Rock, XRF				Sample Count		7	7	7	20	7	15	18	9	2	18	18	24	7	18	15	7	16	7	18	17	23	18	20	24	25	16	18	17	25	18	18	18	23	25	23	

ZP samples from NSW Department of Mineral Resources, Fredrickson & Pecover, 1987

APPENDIX 2 Whole rock trace element analysis of selected zeolitised samples from Currabubula Formation, N.S.W.

SAMPLE NUMBER	SAMP. BY	SiO2 %	TiO2 %	Al2O3 %	Fe2O3 %	FeO %	MnO %	MgO %	CaO %	Na2O %	K2O %	P2O5 %	LOI %	TOTAL %	Ba ppm	Cr ppm	Cu ppm	Ga ppm	Nb ppm	Ni ppm	Pb ppm	Rb ppm	Sr ppm	Th ppm	U ppm	V ppm	Y ppm	Zn ppm	Zr ppm
84McPhie 10	JMcP	70.79	0.19	13.97	1.11	0.44	0.07	0.35	1.89	3.92	3.25	0.04	4.06	100.08	634	8	7	18	9		23	222	239	23	3	8	32	42	130
84McPhie 14	JMcP	74.07	0.26	13.53	1.83	0.21	0.09	0.47	1.38	4.02	3.59	0.04	1.02	100.51	935	9	3	19	7		23	109	191	14		17	17	45	129
84McPhie 15	JMcP	75.25	0.21	12.59	1.20	0.15	0.03	0.28	0.68	2.76	4.96	0.04	1.11	99.26	881	8		17	8		22	171	95	23		12	21	36	135
84McPhie 16	JMcP	75.71	0.17	12.85	1.12	0.09	0.02	0.17	0.61	2.71	5.24	0.04	0.80	99.53	892	7		14	9		15	179	112	27	3	11	32	31	134
84McPhie 17	JMcP	76.15	0.14	12.59	1.05	0.07	0.07	0.12	0.50	3.13	5.10	0.02	0.67	99.61	546	11		16	9		27	201	78	31	3	4	68	32	112
84McPhie 18	JMcP	76.17	0.16	13.22	1.17	0.09		0.30	0.99	3.59	4.27	0.02	0.71	100.69	854	8	3	12	8		23	112	141	14		12	14	32	95
84McPhie 2	JMcP	74.02	0.13	13.11	1.25	0.26	0.01	0.20	0.69	3.20	4.59		2.72	100.18	1410	3	3	19	9	2	22	164	213	11			42	62	197
84McPhie 22	JMcP	71.90	0.31	14.22	1.34	0.08	0.05	0.37	1.81	3.66	3.82	0.06	2.13	99.75	939	7	4	16	8		19	125	237	17		22	21	37	153
84McPhie 23	JMcP	72.75	0.33	14.75	1.73	0.09	0.06	0.33	1.57	4.19	3.71	0.05	1.01	100.57	929	11	3	16	8	2	27	117	295	13	7	26	16	43	156
84McPhie 24	JMcP	73.01	0.29	14.50	1.35	0.08	0.05	0.33	1.32	3.98	3.99	0.05	1.35	100.30	937	7		14	8		24	124	277	15	3	22	16	53	147
84McPhie 25	JMcP	73.22	0.30	14.15	1.45	0.17	0.05	0.32	1.59	4.00	3.93	0.04	0.80	100.02	967	8	2	17	8		15	124	292	17	4	25	16	36	146
84McPhie 26	JMcP	73.43	0.30	14.42	1.27	0.11	0.05	0.25	0.92	3.42	4.68	0.04	1.25	100.14	973	12	3	19	7		21	137	190	21		22	16	42	141
84McPhie 27	JMcP	74.30	0.29	14.17	1.40	0.08	0.04	0.18	1.40	3.85	3.99	0.03	0.91	100.64	962	7		17	8		21	122	264	15		23	15	37	142
84McPhie 28	JMcP	68.47	0.43	13.41	1.05	0.48	0.05	0.31	3.62	3.39	1.04	0.06	7.97	100.28	992	8	4	13	11		26	89	465	19			27	66	358
84McPhie 29	JMcP	71.92	0.26	13.23	0.91	0.21	0.01	0.31	1.79	3.63	3.04	0.04	4.09	99.44	1017	9	4	13	7		15	136	416	15		23	24	36	129
84McPhie 3	JMcP	75.21	0.09	12.65	0.76	0.28		0.13	0.09	1.14	7.38	0.01	2.08	99.82	1090	3	4	18	10	3	8	220	55	18	5		30	57	167
84McPhie 4	JMcP	76.89	0.07	11.96	0.96	0.31	0.02	0.30	0.52	1.81	3.53		3.61	99.98	628		3	18	13	2	7	153	80	18			60	70	164
84McPhie 5	JMcP	75.20	0.08	11.92	0.91	0.16	0.01	0.23	0.45	2.98	2.90	0.02	4.95	99.81	356		4	13	13	2	11	128	112	18	3		35	65	171
84McPhie 6	JMcP	76.11	0.15	12.35	1.66	0.08	0.07	0.04	0.10	4.29	4.28		0.58	99.71	1236	11	2	18	10		21	119	33	15	5		33	84	276
84McPhie 7	JMcP	75.64	0.16	12.50	2.00	0.09	0.07	0.08	0.16	3.97	4.54	0.02	0.82	100.05	1365	10		17	10		26	110	63	15	4	4	26	93	275
84McPhie 8	JMcP	75.44	0.15	12.35	1.65	0.09	0.06	0.10	0.09	4.14	4.36		0.54	98.97	1324	8		18	10		23	121	46	19			23	85	280
84McPhie 9	JMcP	70.28	0.21	14.01	0.96	0.58	0.05	0.36	1.99	3.77	3.38	0.05	4.07	99.71	662	10		17	8		22	208	246	12	3	11	30	52	134
Mean		73.91	0.21	13.29	1.28	0.19	0.05	0.25	1.10	3.43	4.07	0.04	2.15	99.96	933.1	8.3	3.5	16.3	9.0	2.2	20.0	145.0	188.2	16.0	3.9	16.1	27.9	51.6	171.4
Standard Deviation		2.19	0.09	0.87	0.33	0.15	0.02	0.11	0.85	0.78	1.17	0.01	1.91	0.45	262.5	2.4	1.2	2.2	1.7	0.4	5.8	39.0	119.0	4.7	1.3	7.7	14.0	18.8	66.0
No. samples		22	22	22	22	22	20	22	22	22	22	18	22	22	22	20	14	22	22	5	22	22	22	22	11	15	22	22	22

CURRABUBULA FORMATION, Rhyclite Ingnimbrite, Tamworth (9035) 1:100,000 map sheet
Whole Rock samples, U.N.E.
All samples from McPhie, 1984.

APPENDIX 3 Whole rock analysis by McPhie, 1984, of Rhyolite Ignimbrites from the Currabubula Formation.

SAMPLE NUMBER	SAMPLE TYPE	LOCATION	SAMP. BY	AEC meq	SiO_2 %	TiO_2 %	Al_2O_3 %	Fe_2O_3 %	MnO %	MgO %	CaO %	Na_2O %	K_2O %	P_2O_5 %	LOI %	TOTAL %
W8	Rock Chip	Scholfield Creek	JH	147	69.04	0.22	11.58	0.90	0.01	1.19	1.62	1.96	0.86	0.02	12.41	99.82
W9	Rock Chip	Scholfield Creek	JH	151	70.07	0.21	11.39	0.93	0.01	1.20	1.62	1.70	0.96	0.01	12.24	100.35
W10	Rock Chip	Scholfield Creek	JH	149	69.10	0.21	11.65	0.91	0.01	1.08	2.35	1.13	0.91	0.03	12.17	99.55
W11	Rock Chip	4km NE Mowbray	JH	142	70.04	0.16	11.11	0.78	0.02	1.02	1.72	1.23	0.82	0.01	11.98	98.89
		Mean			69.56	0.20	11.43	0.88	0.01	1.12	1.83	1.51	0.89	0.02	12.20	99.65
		Stand Deviation			0.57	0.03	0.24	0.07	0.00	0.09	0.35	0.39	0.06	0.01	0.18	0.61
		Sample Count			4	4	4	4	4	4	4	4	4	4	4	4

SAMPLE NUMBER	As ppm	Ba ppm	Ce ppm	Cr ppm	Cu ppm	Ga ppm	La ppm	Nb ppm	Nd ppm	Ni ppm	Pb ppm	Rb ppm	Sc ppm	Sr ppm	Th ppm	U ppm	V ppm	Y ppm	Zn ppm	Zr ppm
W8	10	2203	55	8	10	13	35	12	28	7	13	18	3	2453	25	9	7	30	35	172
W9	5	2811	56	18	10	15	25	10	31	7	10	18	5	2387	25	5	13	31	38	156
W10	8	6784	36	13	8	13	24	11	23	6	14	21	3	1718	21	5	17	31	34	184
W11	12	9551	48	17	8	9	45	11	39	6	19	20	4	2763	24	7	22	33	16	108
Mean	8.8	5337.3	48.8	14.0	9.0	12.5	32.3	11.0	30.3	6.5	14.0	19.3	3.8	2330.3	23.8	6.5	14.8	31.3	30.8	155.0
Stand Deviation	3.0	3466.7	9.2	4.5	1.2	2.5	9.8	0.8	6.7	0.6	3.7	1.5	1.0	439.9	1.9	1.9	6.3	1.3	10.0	33.4
Sample Count	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4

NEAR WILLOWS, Ducabrook Formation, Drummond Basin, Qld.
All Whole rock, Analysis by P. Flood, U.N.E.
AEC > 70 meq/100g

APPENDIX 4 Whole rock analysis zeolite sample from near Willows, Ducabrook Formation, Drummond Basin, Qld.

SAMPLE NUMBER	SAMPLE TYPE	LOCATION	SAMP. BY	BATCH	ASSAYED MATERIAL	SiO_2 %	TiO_2 %	Al_2O_3 %	Fe_2O_3 %	MnO %	MgO %	CaO %	Na_2O %	K_2O %	TOTAL %	LAB
W2	Rock Chip	Willows, Qld.	JH	1993 - 1	Core bladed shard	66.39	0.30	16.98	0.98	<0.12	0.51	4.87	0.29	1.35	91.67	U.N.E.
W2	Rock Chip	Willows, Qld.	JH	1993 - 2	Core bladed shard	67.93	0.10	15.43	2.15	<0.12	0.94	4.33	0.34	1.11	92.46	U.N.E.
W2	Rock Chip	Willows, Qld.	JH	1993 - 3	Core bladed shard	66.22	0.19	16.43	0.57	<0.12	1.18	4.48	0.18	1.01	90.26	U.N.E.
W2	Rock Chip	Willows, Qld.	JH	1993 - 4	Core bladed shard	66.42	0.10	16.71	0.55	<0.12	0.77	4.63	0.17	1.33	90.56	U.N.E.
W2	Rock Chip	Willows, Qld.	JH	1993 - 7	Core bladed shard	66.43	0.14	15.68	0.10	<0.12	1.00	4.17	0.22	0.99	88.57	U.N.E.
W2	Rock Chip	Willows, Qld.	JH	1993 - 8	Core bladed shard	66.99	0.16	16.19	0.10	<0.12	1.33	4.86	0.10	1.14	90.57	U.N.E.
W2	Rock Chip	Willows, Qld.	JH	1993 - 9	Core bladed shard	66.86	0.10	14.05	1.89	<0.12	0.61	3.80	0.22	0.87	88.58	U.N.E.
W2	Rock Chip	Willows, Qld.	JH	1993 - 10	Core bladed shard	68.79	0.10	14.33	0.30	<0.12	0.77	3.97	0.10	0.93	89.14	U.N.E.
W2	Rock Chip	Willows, Qld.	JH	1993 - 11	Core bladed shard	66.41	0.17	20.46	0.52	<0.12	0.77	3.81	0.47	1.09	93.70	U.N.E.
W2	Rock Chip	Willows, Qld.	JH	1993 - 12	Core bladed shard	66.95	0.16	17.28	0.24	<0.12	0.70	4.71	0.29	1.49	91.07	U.N.E.
W2	Rock Chip	Willows, Qld.	JH	1993 - 13	Core bladed shard	63.92	0.25	16.46	0.76	<0.12	0.88	4.67	0.16	1.12	88.07	U.N.E.
W2	Rock Chip	Willows, Qld.	JH	1993 - 14	Core bladed shard	68.00	0.40	15.48	0.10	<0.12	1.09	4.60	0.23	1.11	91.41	U.N.E.
W2	Rock Chip	Willows, Qld.	JH	1993 - 15	Core bladed shard	64.27	0.17	15.76	0.15	<0.12	0.77	4.48	0.16	1.10	86.71	U.N.E.
W2	Rock Chip	Willows, Qld.	JH	1993 - 16	Core bladed shard	68.79	0.18	17.16	0.14	<0.12	1.08	4.57	0.24	1.33	93.34	U.N.E.
W2	Rock Chip	Willows, Qld.	JH	1993 - 17	Core bladed shard	61.44	0.37	15.48	0.14	<0.12	0.47	4.84	0.16	1.55	84.35	U.N.E.
W2	Rock Chip	Willows, Qld.	JH	1993 - 24	Core bladed shard	66.59	0.17	15.68	0.41	<0.12	1.03	4.63	0.16	0.77	89.28	U.N.E.
W2	Rock Chip	Willows, Qld.	JH	1993 - 25	Core bladed shard	68.07	0.12	13.79	0.78	<0.12	0.55	3.82	0.16	1.11	88.12	U.N.E.
W2	Rock Chip	Willows, Qld.	JH	1993 - 26	Core bladed shard	64.71	0.19	17.02	3.61	<0.12	0.14	4.86	0.44	1.76	92.72	U.N.E.
W2	Rock Chip	Willows, Qld.	JH	1993 - 27	Core bladed shard	67.98	0.54	17.02	0.60	<0.12	0.12	5.30	0.25	1.65	93.33	U.N.E.
W2	Rock Chip	Willows, Qld.	JH	1993 - 28	Core bladed shard	65.49	0.31	17.31	1.77	<0.12	1.09	4.31	0.25	1.37	91.90	U.N.E.
W2	Rock Chip	Willows, Qld.	JH	1993 - 29	Core bladed shard	68.15	0.15	16.50	0.33	<0.12	1.19	4.53	0.29	1.29	92.42	U.N.E.
W2	Rock Chip	Willows, Qld.	JH	1993 - 5	Rim bladed shard	68.43	<0.12	15.22	0.38	<0.12	1.02	4.38	0.21	0.86	90.51	U.N.E.
W2	Rock Chip	Willows, Qld.	JH	1993 - 6	Rim bladed shard	68.17	<0.12	15.00	0.16	<0.12	0.66	4.40	0.16	1.17	89.57	U.N.E.
W2	Rock Chip	Willows, Qld.	JH	1993 - 1G	Groundmass	79.49	<0.12	14.21	1.50	<0.12	0.68	1.69	0.16	0.72	98.30	U.N.E.
W2	Rock Chip	Willows, Qld.	JH	1993 - 2G	Groundmass	88.07	<0.12	11.58	0.54	<0.12	0.25	1.11	0.15	0.35	101.89	U.N.E.
M34187	Crystals	Phillip Island, Vic.		Birch,1989, p.97	Crystal	58.54		13.06	0.04		1.61	2.52	1.59	1.72	79.16	Melb Uni
M34187	Crystals	Phillip Island, Vic.		Birch,1989, p.97	Crystal	61.71		13.36	0.04		1.55	2.79	1.46	1.42	82.64	Melb Uni
M13643	Crystals	Maldon, Vic.		Birch,1989, p.97	Crystal	59.42		15.16	0.11		2.11	4.85	0.22	0.56	82.65	Melb Uni
MATERIAL SUBTOTALS		WILLOWS, CORE SHARD			Mean	66.51	0.21	16.25	0.77	0.00	0.81	4.49	0.23	1.21	90.39	
					Stand Deviation	1.79	0.12	1.42	0.89	0.00	0.33	0.40	0.10	0.26	2.42	
					Sample Count	21	21	21	21	21	21	21	21	21	21	
		WILLOWS, RIM SHARD			Mean	68.30	<0.12	15.11	0.27	0.00	0.84	4.39	0.18	1.01	90.04	
					Stand Deviation	0.18	0.00	0.16	0.16	0.00	0.25	0.01	0.04	0.22	0.66	
					Sample Count	2	2	2	2	2	2	2	2	2	2	
		WILLOWS, GROUNDMASS			Mean	83.78	<0.12	12.89	1.02	0.00	0.47	1.40	0.16	0.54	100.10	
					Stand Deviation	6.07	0.00	1.86	0.68	0.00	0.30	0.41	0.01	0.26	2.54	
					Sample Count	2	2	2	2	2	2	2	2	2	2	
		VICTORIA, HYDROTHERMAL CRYSTALS			Mean	59.89		13.86	0.06		1.76	3.39	1.09	1.23	81.48	
		(Heulandite, Microprobe)			Stand Deviation	1.64		1.14	0.04		0.31	1.27	0.76	0.60	2.01	
					Sample Count	3	0	3	3	0	3	3	3	3	3	
WILLOWS, QLD (sample W2)			ALL ANALYSIS		Mean	68.04	0.17	15.89	0.75	0.00	0.78	4.23	0.22	1.14	91.14	
Microprobe analysis by P. Flood, U.N.E.					Stand Deviation	5.19	0.13	1.65	0.84	0.00	0.32	0.93	0.09	0.31	3.53	
W2 AEC = 100 meq/100g, Fe is sum total					Sample Count	25	25	25	25	25	25	25	25	25	25	

APPENDIX 5 Microprobe analysis of zeolitised sample from Willows, Ducabrook Formation, Drummond Basin. Analysis by P. Flood, U.N.E.

SAMPLE NUMBER	SAMPLE TYPE	LOCATION	BATCH	ASSAYED MATERIAL	SiO2 %	Al2O3 %	FeO %	MnO %	MgO %	CaO %	Na2O %	K2O %	TOTAL %
R17685	Drill Chips	Moorbannool Bore 8, 129m	Duddy'88,Table9.3-15	Crystal	63.69	15.15	0.16		1.23	3.11	0.55	1.33	86.40
R17685	Drill Chips	Moorbannool Bore 8, 129m	Duddy'88,Table9.3-16	Crystal	62.91	15.73	0.20	0.05	1.27	2.99	0.41	1.47	85.71
R17685	Drill Chips	Moorbannool Bore 8, 129m	Duddy'88,Table9.3-17	Crystal	65.35	15.48	0.18	0.03	1.44	3.20	0.15	1.28	87.69
R17685	Drill Chips	Moorbannool Bore 8, 129m	Duddy'88,Table9.3-18	Crystal	63.42	14.95	0.16		1.61	3.21	0.39	1.72	86.51
R17685	Drill Chips	Moorbannool Bore 8, 129m	Duddy'88Table9.3-19	Crystal	65.58	15.36	0.20		1.61	3.08	0.16	1.38	87.86
R25078	Drill Chips	Yangery 1, 976m	Duddy'88,Table9.5-10	Crystal	61.49	14.65	0.35		0.68	3.68	0.41	0.32	84.12
R25078	Drill Chips	Yangery 1, 976m	Duddy'88,Table9.5-11	Crystal	61.94	14.75	0.95		0.98	3.70	0.35	0.29	85.35
R25078	Drill Chips	Yangery 1, 976m	Duddy'88,Table9.5-12	Crystal	63.20	14.97	0.10		0.48	3.85	0.47	0.28	86.19
R25078	Drill Chips	Yangery 1, 976m	Duddy'88,Table9.5-13	Crystal	62.47	14.68	0.22		0.38	3.97	0.64	0.26	85.23
R25078	Drill Chips	Yangery 1, 976m	Duddy'88,Table9.5-9	Crystal	63.46	14.84	0.27	0.07	0.43	3.81	0.32	0.20	85.82
R25087	Drill Chips	Corriejong 1, 1096m	Duddy'88,Table9.5-14	Crystal	59.88	17.37	0.09	0.04	0.13	3.73	0.33	0.25	87.98
R25087	Drill Chips	Corriejong 1, 1096m	Duddy'88,Table9.5-15	Crystal	62.67	15.04	0.23		0.32	3.74	0.70	0.31	88.92
R25194	Drill Chips	Yangery 1, 922m	Duddy'88,Table9.5-8	Crystal	59.26	15.31	0.21	0.25	0.91	5.03	0.37	0.59	84.78
R25312	Drill Chips	Gerangamete 13, 556m	Duddy'88,Table9.5-6	Crystal	60.48	17.24	0.37	0.03	1.24	2.52	0.56	1.50	86.40
R25312	Drill Chips	Gerangamete 13, 556m	Duddy'88,Table9.5-7	Crystal	58.76	17.49	0.19	0.05	1.39	3.22	0.40	1.31	85.48
R25321	Drill Chips	Tullich 1, 166m	Duddy'88,Table9.5-1	Crystal	63.25	15.45	0.16	0.04	1.05	1.93	1.27	1.74	85.70
R25321	Drill Chips	Tullich 1, 166m	Duddy'88,Table9.5-2	Crystal	62.11	15.96	0.26		1.06	2.23	3.14	1.70	87.32
R25321	Drill Chips	Tullich 1, 166m	Duddy'88,Table9.5-3	Crystal	62.47	15.21	0.15		1.04	2.12	1.57	1.35	84.82
R25321	Drill Chips	Tullich 1, 166m	Duddy'88,Table9.5-4	Crystal	63.51	14.36	0.12		1.18	1.78	1.11	1.87	84.49
R25321	Drill Chips	Tullich 1, 166m	Duddy'88,Table9.5-5	Crystal	61.22	15.67	0.34		1.12	2.06	1.78	1.80	85.21
R26419	Drill Chips	Flaxman's 1, 2350m	Duddy'88,Table9.5-16	Crystal	59.34	14.72	0.68			5.61	0.33	0.29	86.76
R26419	Drill Chips	Flaxman's 1, 2350m	Duddy'88,Table9.5-17	Crystal	57.81	15.93	0.50			5.53	0.60	0.28	85.65
R25020	Rock Chip	Loc. 65	Duddy'83,Table9.3-5	Crystal	62.24	15.02	0.20		1.23	3.94	0.38	1.52	84.53
R25020	Rock Chip	Loc. 65	Duddy'83,Table9.3-6	Crystal	61.27	14.96	0.34	0.04	1.35	3.57	9.41	1.58	83.72
R25020	Rock Chip	Loc. 65	Duddy'83,Table9.3-7	Crystal	66.13	15.57	0.44	0.07	0.52	3.16	0.38	1.59	88.86
R25020	Rock Chip	Loc. 65	Duddy'83,Table9.3-8	Crystal	62.97	15.28	0.21	0.06	0.21	4.21	0.39	1.83	86.47
R25020	Rock Chip	Loc. 65	Duddy'83,Table9.3-9	Crystal	62.89	14.89	0.63	0.03	0.52	3.70	0.89	1.66	86.46
R25287	Rock Chip	Loc. 157A	Duddy'83,Table9.3-10	Crystal	59.95	14.96	0.26	0.06	0.54	3.74	0.18	1.66	85.65
R25287	Rock Chip	Loc. 157A	Duddy'83,Table9.3-11	Crystal	59.03	15.92	0.10		0.44	3.36	0.13	1.46	86.17
R25287	Rock Chip	Loc. 157A	Duddy'83,Table9.3-12	Crystal	61.45	14.65	0.12		0.32	3.87	0.24	1.42	87.92
R25373	Rock Chip	Loc. 204	Duddy'83,Table9.3-13	Crystal	59.49	15.27	0.12		1.29	2.68	2.03	2.59	84.63
R25373	Rock Chip	Loc. 204	Duddy'83,Table9.3-14	Crystal	59.18	16.15			1.40	2.66	2.23	2.01	84.85
R26441	Rock Chip	Loc. 15	Duddy'83,Table9.3-1	Crystal	57.86	16.49	0.37		1.38	2.86	1.74	2.46	84.04
R26441	Rock Chip	Loc. 15	Duddy'83,Table9.3-2	Crystal	59.96	16.35	0.35	0.05	1.47	1.96	1.19	2.70	82.09
R26441	Rock Chip	Loc. 15	Duddy'83,Table9.3-3	Crystal	59.19	15.06	1.08	0.14	1.31	1.56	1.59	2.99	84.36
R26458	Rock Chip	Loc. 30	Duddy'83,Table9.3-4	Crystal	59.15	16.03	0.09		0.97	1.87	2.41	0.85	84.12
R19335	Rock Chip	Loc. 153	Duddy'83,Table9.4-3	Crystal in Concretion	59.70	14.74		0.05	1.10	1.76	2.76	3.29	84.35
R19335	Rock Chip	Loc. 153	Duddy'83,Table9.4-4	Crystal in Concretion	63.10	15.25	0.10		1.23	1.83	2.07	4.58	88.92
R19335	Rock Chip	Loc. 153	Duddy'83,Table9.4-5	Crystal in Concretion	62.90	15.06	0.11	0.08	0.97	1.91	2.41	3.30	87.01
R25139	Rock Chip	Loc. 14	Duddy'83,Table9.4-10	Crystal in Concretion	62.52	14.63	0.16	0.03	1.33	3.45	0.47	0.92	84.13
R25139	Rock Chip	Loc. 14	Duddy'83,Table9.4-11	Crystal in Concretion	61.83	14.50	0.14	0.05	1.42	3.39	0.37	1.37	83.22
R25139	Rock Chip	Loc. 14	Duddy'83,Table9.4-12	Crystal in Concretion	59.44	15.01	0.14	0.22	1.45	5.20	0.66	1.83	84.31
R25139	Rock Chip	Loc. 14	Duddy'83,Table9.4-9	Crystal in Concretion	61.82	14.77	0.11	0.16	1.39	5.49	0.59	1.56	86.24
R25366	Rock Chip	Loc. 204	Duddy'83,Table9.4-7	Crystal in Concretion	65.12	14.54	0.19	0.07	1.21	0.96	2.31	3.14	87.85
R25366	Rock Chip	Loc. 204	Duddy'83,Table9.4-8	Crystal in Concretion	63.38	15.23	0.69	0.09	1.14	1.63	4.03	1.77	88.36
R26491	Rock Chip	Loc. 110	Duddy'83,Table9.4-6	Crystal in Concretion	68.69	13.30	0.87	0.09	0.36	0.36	2.79	2.19	88.68
R26640	Rock Chip	Loc. 194	Duddy'83,Table9.4-1	Crystal in Concretion	65.99	14.09	0.03	0.09	0.97	4.39	0.13	1.54	87.96
R26640	Rock Chip	Loc. 194	Duddy'83,Table9.4-2	Crystal in Concretion	63.83	13.73	0.62	0.10	0.91	4.52	0.06	0.98	85.30
MATERIAL SUBTOTALS		CRYSTALS, DRILL HOLES		Mean	62.01	15.47	0.28	0.07	0.98	3.37	0.73	0.98	86.07
				Stand Deviation	2.05	0.88	0.20	0.07	0.44	1.07	0.69	0.65	1.19
				Sample Count	22	22	22	8	20	22	22	22	22
		CRYSTALS, SURFACE		Mean	60.77	15.47	0.33	0.06	0.92	3.08	1.66	1.88	85.28
				Stand Deviation	2.20	0.61	0.27	0.04	0.47	0.84	2.38	0.59	1.78
				Sample Count	14	14	13	7	14	14	14	14	14
		CRYSTALS IN CONCRETIONS (SURFACE)		Mean	63.19	14.57	0.29	0.09	1.13	2.91	1.55	2.21	86.37
				Stand Deviation	2.57	0.60	0.29	0.05	0.30	1.72	1.32	1.13	2.02
				Sample Count	12	12	11	11	12	12	12	12	12
OTWAY BASIN (DUDDY, 1983), Vic.			ALL SAMPLES	Mean	61.94	15.25	0.29	0.08	1.00	3.17	1.21	1.55	85.91
All microprobe analysis, Melb. Uni.				Stand Deviation	2.36	0.83	0.24	0.06	0.42	1.20	1.54	0.94	1.63
Clinoptilolite-Heulandite crystals.				Sample Count	48	48	46	26	46	48	48	48	48

APPENDIX 6 Microprobe analysis by Duddy, 1983, of zeolite crystals from Otway Formation, Otway Basin, Victoria.